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THE PYROLYSIS OF CARBON COMPOUNDS

BY

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American Chemical Society
Monograph Series

BOOK DEPARTMENT

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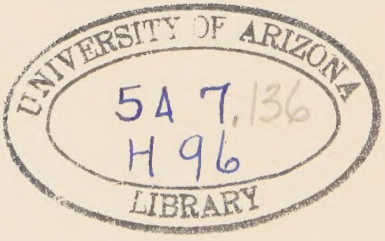

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

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Preface

Twenty-three centuries ago Empedocles recognized fire as one of the "four elements," the other three being earth, air and water. Fire, as the agent for destructive distillation, was a favorite tool of the alchemist. Although the general prevalence of such reactions of pyrolysis has long been recognized, it is in the last six decades that the subject has assumed a scientific basis. Since many of the recorded data on thermal decompositions have been incidental observations, it is apparent that the information is widely scattered throughout the literature. The mere fact that the records of many melting-point determinations are accompanied by the trite expression "It melts with decomposition" is sufficient evidence that the subject of pyrolysis has had an unorganized past.

In planning this monograph, therefore, the two primary motives were the provision of as complete a survey as possible of the pertinent literature (to include the entire 1928 *Chemical Abstracts*), and the rational organization of this material. Because of the voluminous nature of the literature of organic chemistry, it is reasonably certain that the monograph cannot be entirely complete, although no cases have been wilfully omitted. The generous cooperation of several workers in the field has enabled the author to include much unpublished material.

In general, it has been possible to arrange the compounds in the order of their functional groups, and to retain the sequence: hydrocarbons, alkyl halides, alcohols, aldehydes, etc., which is familiar in most texts of general organic chemistry. In addition, many cross-references have been included. Compounds for which a transient, but non-isolable, existence is assumed during the course of a given reaction are so indicated by brackets; thus, [ ]. A compilation of several satisfactory synthetic methods is given in the index under the heading "Preparations." The abbreviations used are those of the American Chemical Society.

The author is particularly indebted to Professor Frank C. Whitmore of Northwestern University for his active interest at the start of this undertaking and for many helpful features during the progress of the work. The author was ably assisted by his wife in the preparation of the index. He also wishes to express his gratitude to Professor C. S.

Hamilton (Northwestern), Professor Howard J. Lucas (California Institute of Technology), Dr. Robert N. Pease (Princeton), and Dr. F. W. Sullivan, Jr. (Standard Oil Co. of Indiana) for constructive criticism of various portions of the manuscript.

CHARLES D. HURD

Evanston, Illinois
March, 1929.

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kind must always be used and catalysis enthusiasts are becoming more and more convinced that much which was not thought to be catalytic is now included in its scope. To illustrate, it has been thought that the presence of different kinds of glass in glass apparatus sometimes is the cause for anomalous results. However, in high-temperature reactions where catalytic agents of demonstrated value are absent, the viewpoint has been taken in this monograph that such reactions should be classified as reactions of pyrolysis and not catalysis. For reactions of the latter type, the reader is referred to Sabatier's excellent treatise, "Catalysis in Organic Chemistry", of which the American edition (D. VanNostrand Co.) is translated by E. E. Reid.

Glass, quartz or porcelain surfaces are the ones which are most used in laboratory pyrolyses. Their catalytic action is, at the best, very slight. In larger scale work, it is usually necessary to resort to metallic surfaces. Wilson and Bahlke [2] have recently reported that in cracking stills, it is best to use chromium-steels ("stainless" steels), or aluminum or calorized iron. Copper and some bronzes are not satisfactory, neither does monel appear to be advantageous. These authors were interested in corrosion, which occurs especially above 315° C. (600° F.) and which is due to hydrogen sulfide and other sulfur compounds. Franz Fischer [3] has performed many pyrogenic experiments in a tinned-iron tube, which would have failed in an iron tube because of carbon deposition or other causes. Thus, at 800°, cresol was reduced by hydrogen to benzene and toluene, and aniline to benzene and ammonia, the latter reaction in 90 per cent yields. The same author has shown [4] that a ferrous sulfide inner lining in an iron tube also prevents carbon deposit in these reactions. The sulfide layer is formed by passing hydrogen sulfide through the tube.

[2] Wilson and Bahlke, *Ind. Eng. Chem.* **17**, 355 (1925).
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[4] Fischer and Zerbe, *Brennstoff-Chem.* **4**, 309 (1923); *Chem. Abstracts* **18**, 674 (1924).

Chapter 2.

Generalizations.

Rule of Least Molecular Deformation.

This rule states that the decomposition by heat will follow that reaction which requires the least possible deformation of the molecule. Thus, at higher temperatures, when a compound gives a series of endothermic reactions or feebly exothermic ones, the atomic bonds in the resultant new compounds tend to be as nearly identical as possible with those in the original compound.[1] This is well illustrated by the following reactions, the details of which will be presented later:

(1) $$2C_6H_6 \longrightarrow C_6H_5—C_6H_5 + H_2.$$

In this pyrogenic reaction, the gases are over 90 per cent hydrogen.

(2) $$H—CO—O—CH_3 \longrightarrow 2H—CO—H.$$

Formaldehyde is thus formed if the ester is passed rapidly. At a slower rate, the aldehyde is decomposed also into hydrogen and carbon monoxide. A pyrolysis entirely in accord [2] with this is the formation of small amounts of phosgene at the boiling point of trichloromethyl chloroformate:

$$Cl—CO—O—CCl_3 \longrightarrow 2COCl_2.$$

(3) $$CH_3—CHO \longrightarrow CH_4 + CO,$$

as a dominant reaction, with

$$2CH_3—CHO \longrightarrow C_2H_4 + 2H_2 + 2CO$$

as a secondary reaction.

(4) $$CH_3OH \longrightarrow H_2 + HCHO.$$

Mlle. Peytral proved that the formation of $CO + 2H_2$ is a secondary reaction by showing that the ratio $CO : HCHO$ increases with the time of heating.

Many other reactions could be selected to illustrate this generalization. For example,[3] in the dry distillation of lysidine hydrochloride,

[1] Peytral, *Compt. rend.* **165**, 703 (1917); **179**, 831 (1924); *Bull. soc. chim.* **27**, 34 (1920); **29**, 44 (1921).
[2] Grignard, Rivat and Urbain, *Compt. rend.* **169**, 1074 (1919).
[3] Ladenburg, *Ber.* **28**, 3069 (1895).

THE PYROLYSIS OF CARBON COMPOUNDS

Chapter 1.

Pyrolysis.

The transformation of a compound into another substance, or into other substances, through the agency of heat alone is called pyrolysis. Frequently, pyrolyses are thermal decompositions, but the term "Pyrolysis" is somewhat broader than "Thermal Decomposition". Also, it is more concise. In "decompositions", there is always the implication of the formation of at least two simpler substances. In pyrolyses, this is not always the case. For example, rearrangements may be caused by heat alone. Furthermore, the formation of large molecules from smaller ones is often effected by heat. Both of these changes are pyrolytic ones, but it would be awkward to classify them as decompositions.

Our conception of hot and cold is strictly a relative one. Some compounds decompose at the temperature of boiling water, whereas others require red heat. Similarly, compounds may be stable at — 40° but not at 0°. All of these changes, if caused by temperature alone, are examples of pyrolysis. To be sure, the great majority of pyrolyses occur at "high" temperatures, but this only means that our familiarity with compounds which cannot exist at ordinary temperatures is, relatively, extremely limited.

It would exceed the scope of the present monograph to develop the subject of catalysis in its relation to pyrolysis. Occasionally, however, it will be helpful to note the effect of catalysts, but no systematic effort will be made in this direction. Frequently in thermal decompositions, it is difficult to distinguish between the catalytic and the non-catalytic. As Stieglitz [1] has remarked, "truly catalytic actions must merge by imperceptible degrees into truly non-catalytic actions and there is no dividing line possible at any point". It is obvious that apparatus of some

[1] Stieglitz, *Am. Chem. J.* **39**, 427 (1908).

kind must always be used and catalysis enthusiasts are becoming more and more convinced that much which was not thought to be catalytic is now included in its scope. To illustrate, it has been thought that the presence of different kinds of glass in glass apparatus sometimes is the cause for anomalous results. However, in high-temperature reactions where catalytic agents of demonstrated value are absent, the viewpoint has been taken in this monograph that such reactions should be classified as reactions of pyrolysis and not catalysis. For reactions of the latter type, the reader is referred to Sabatier's excellent treatise, "Catalysis in Organic Chemistry", of which the American edition (D. VanNostrand Co.) is translated by E. E. Reid.

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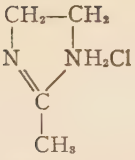
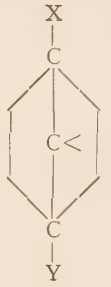


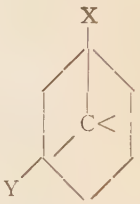
, there is formed acetylene, acetonitrile and ammonium chloride. The elimination of carbon dioxide from acids is a very familiar illustration. Although the rule is frequently useful, it may be said in criticism, that in many cases, prior to an experiment, it would be difficult to decide which plan of rupture would involve the least deformation of the molecule. Thus, who would predict that the groupings $\equiv C—CH_2OH$ and $=N—CH_2OH$ pyrolyze differently? The former changes into $\equiv C—CHO + H_2$, and the latter into $=NH + CH_2O$. Or, what is the least molecular deformation in the cracking of hydrocarbons? This rule furnishes no clue to enable one to locate the position of scission in a carbon chain. Many other examples, which would further bear out this contention, may be selected from the illustrations in this book. However, the rule does emphasize the important fact that there is a relationship, often a predictable one, between the original compound and the products of its pyrolysis.

Bredt's Rule.

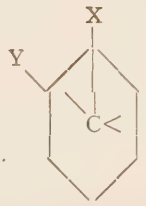
This rule is much less general. Bredt [4] noted that in cyclic structures related to camphane and pinane, such as



or

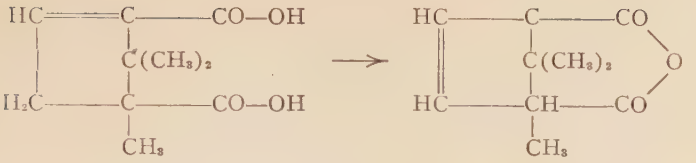


(but not to carane)

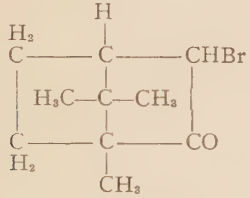


, the carbon atoms in the nucleus labelled X and Y are not capable of holding a double bond. Bredt cited several facts to show the correctness of his rule. Thus, dehydrocamphoric acid cannot form an anhydride by dry distillation. Instead, there is formed the product of rearrangement, *iso*dehydrocamphoric anhydride:

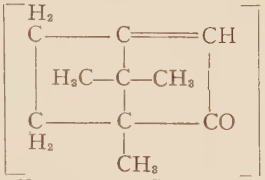
[4] Bredt, Thovet and Schmitz, *Ann.* **437**, 1 (1924).



Again, bromocamphor clings tenaciously to its H and Br and cannot be made to form the unsaturated compound by treatment with alcoholic potash.

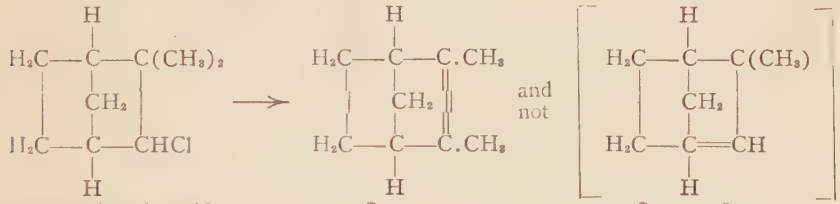


Bromocamphor



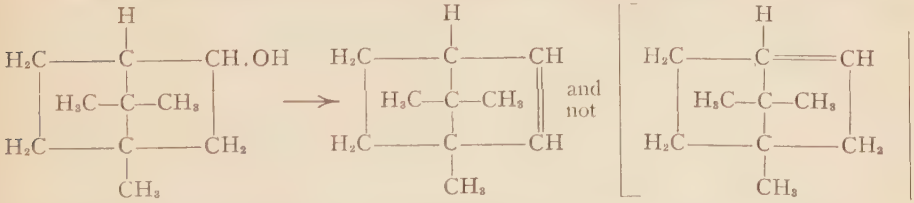
Unsaturated Compound

Similarly, camphenilyl chloride gives santene and not the isomer. This reaction involves a curious migration of the methyl group. Thus:



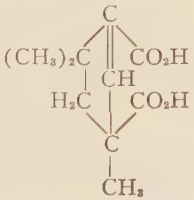
Camphenilyl Chloride *Santene* *Santene Isomer*

When epiborneol is dehydrated, bornylene is produced as it should be:



Epiborneol *Bornylene*

Toivonen[5] has shown the impossibility of anhydride formation with dehydro*iso*fencho-carboxylic acid,

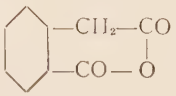


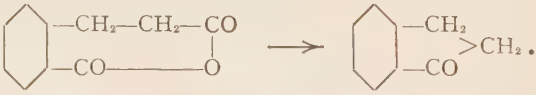
, although it is of

[5] Toivonen, *Ann.* **419**, 200 (1919).

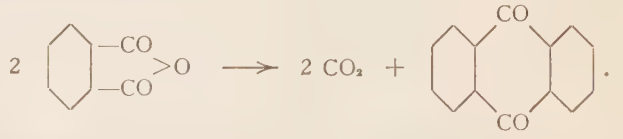
the glutaconic acid type. In a study of the conditions for ring formation when ketonic acids (*see* p. 359) are heated, Windaus and Bohne [6] have made use of Bredt's rule. Concerning *meta* and *para* ring closures, see pp. 293 and 309-310.

Blanc's Rule.

Blanc's rule has also been of assistance in the determination of structure. Blanc discovered [7] that cyclic anhydrides related to adipic and pimelic acids lose carbon dioxide and give good yields of cyclic pentanones and hexanones when distilled at atmospheric pressure. Inasmuch as the dibasic acids related to glutaric and succinic acids yield only the anhydrides by heat, it is not surprising that this test has frequently been used to elucidate the structure of such compounds. It has recently been shown [8] that this rule holds when a hexamethylene ring is a part of the system. For example, either the *cis* or the *trans* anhydride of hexahydrohomophthalic acid,  , reverts to an equilibrium mixture of the two, when heated for 12 hours at 220°, but carbon dioxide is not eliminated. However, the homolog of this anhydride yields hexahydro-α-hydrindone at 240-260°.



Cis-hexahydrophthalic anhydride, which is related structurally to succinic anhydride, has been found [9] to liberate carbon dioxide at 380°. From this, it seems that the mere elimination of carbon dioxide is not sufficient evidence if the rule is to be used as a means of proving structure (*see* p. 405). In this case, the following reaction applies:

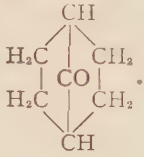


However, it may be noted that most substituted adipic or pimelic anhydrides undergo ketone formation at temperatures below 300°.

An interesting case which combines Bredt's and Blanc's rule is the comparison of terephthalic acid and hexahydroterephthalic acid. The former sublimes without decomposition; heating with chalk liberates

[6] Windaus and Bohne, *Ann.* **442**, 7 (1925).
[7] Blanc, *Compt. rend.* **144**, 1356 (1907).
[8] Windaus, Huckel and Reverey, *Ber.* **56**, 91 (1923).
[9] Windaus and Ehrenstein, *Nachr. Göttingen* **1922**, 1-7; *Chem. Abstracts* **17**, 1431 (1923).

carbon dioxide and benzene, but gives no cyclic ketone. If the barium salt of hexahydroterephthalic acid [10] is distilled with calcium carbonate, there is produced a small yield of a ketone, which is considered to be

bicyclo-1,2,2-heptanone,  .

Haber's Rule.

Another generalization, the credit for which goes to Haber,[11] is that the C—C linkage in the aromatic series is more stable than the C—H linkage, the reverse of which is true in the aliphatic series. To illustrate this rule, Haber found that hexane, if heated for a short time at 600° C., decomposes chiefly into methane, and amylene, ethylene and propylene. A much higher temperature is necessary for the liberation of hydrogen. At 1200°, hexane decomposes largely into carbon and hydrogen. More recently, Calingaert [12] has subjected both *n*- and *iso*-pentane to pyrogenic decomposition at 600°, and found but little hydrogen. The carbon-to-carbon chain becomes severed preferentially. Similarly, *iso*butane [13] gives chiefly methane and propylene as it breaks down at 600°.

The dealkylation of aromatic compounds, when reduced by hydrogen [14] at elevated temperatures, is in agreement with Haber's rule. Fischer noted that the stability of the benzene homologs decreases rapidly in the presence of hydrogen as the molecular weight increases.

Benzene is far more resistant to heat than is hexane. When benzene is broken down, however, hydrogen is eliminated and diphenyl is formed. This differs quite materially from the behavior of hexane. In a similar way, dinaphthyl may be synthesized from naphthalene, fluorene from diphenylmethane, phenanthrene from stilbene, and carbazole from diphenylamine. These illustrations and others will be expounded later in more detail.

Haber's rule meets many embarrassing situations. Both methane and ethane yield hydrogen on pyrolysis. Methane, of course, cannot change into a simpler hydrocarbon. Were methane and ethane the only exceptional cases, Haber's rule would still be very useful. However, the fact that hydrogen is frequently an important reaction product from higher aliphatic hydrocarbons speaks strongly against a rigid interpre-

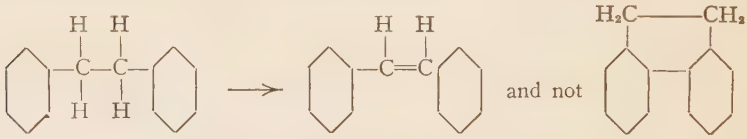
[10] Zelinsky, *Ber.* **34**, 3798 (1901).
[11] Haber, *Ber.* **29**, 2694 (1896).
[12] Calingaert, *J. Am. Chem. Soc.* **45**, 130 (1923).
[13] Hurd and Spence, unpublished results.
[14] Fischer and Schrader, *Brennstoff-Chem.* **1**, 22 (1920); *Chem. Abstracts* **15**, 590 (1921).

tation of the rule. Thus, a recent patent describes the preparation of propylene from propane (p. 65), and the hydrogen output from hexadecane at about 600° is quite marked (p. 74). The rule fails more completely in the case of unsaturated aliphatic compounds. Ethylene, for example, produces as high as 1 percent of divinyl (p. 60), at high temperatures:

$$2C_2H_4 \longrightarrow C_4H_6 + H_2 .$$

This is precisely analogous to the formation of diphenyl from benzene. Butylene cracks into smaller hydrocarbons (p. 78), but there is also a slight dehydrogenation into divinyl. At 750°, isoprene gives 33 percent of gaseous products, one-quarter of which is hydrogen (p. 86).

The behavior of aromatic compounds with side chains is also of interest in this connection. *p*-Chlorotoluene changes into symmetrical di-*p*-chlorophenyl ethane (p. 144), and other halogenated derivatives of toluene behave similarly. Thus, *m*-fluorotoluene yields symmetrical di-*m*-fluorophenyl ethane, $F—C_6H_4—CH_2—CH_2—C_6H_4F$. With only Haber's rule as a guide, one would have predicted a different type of reaction for these compounds since they possess both aliphatic and aromatic hydrogens. With Haber's rule, one would have anticipated derivatives of diphenyl instead of derivatives of ethane. Similarly, this rule is misleading in the pyrolysis of symmetrical diphenyl ethane (p. 98). Two aliphatic hydrogens are eliminated instead of two aromatic hydrogens. Stilbene is the isolated product. Thus:



Finally, another limitation of Haber's rule is that it fails to treat alicyclic compounds, such as cyclohexane, etc. (p. 89).

Berthelot's Theory of Pyrogenic Reactions.

Berthelot [15] was one of the pioneers in the field of thermal decompositions. Over 60 years ago, he observed that methane and ethane pyrolyzed with the liberation of hydrogen. His studies also included certain aromatic hydrocarbons, and a rather superficial treatment of pentane and amylene. Acetylene was investigated in considerable detail. To explain his results, Berthelot proposed the following theory, which,

[15] Berthelot, *Ann. chim. phys.* [4] 9, 445-483 (1866); 12, 143-187 (1867).

unfortunately, he considered to be of general application. The theory is divided into three parts.

1. In addition to pyrolytic reactions of decomposition, there are also reactions of synthesis. In the latter, there is progressive hydrogen elimination, accompanied by the gradual formation of complex hydrocarbons, which eventually may result in the deposition of carbon.

2. The building-up processes and the tearing-down processes are considered to limit each other since the higher hydrocarbons which are produced decompose in turn, and since the lower ones are changed into higher. This leads to a complicated equilibrium between an increasing number of hydrocarbons. Berthelot's conception of the decomposition of methane is as follows:

$$2CH_4 \longrightarrow CH_2{=}CH_2 + 2H_2$$
$$2CH_4 \longrightarrow CH{\equiv}CH + 3H_2$$
$$CH_2{=}CH_2 \longrightarrow CH{\equiv}CH + H_2$$
$$CH{\equiv}CH + H_2 \longrightarrow CH_2{=}CH_2$$
$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3$$
$$2CH_3{-}CH_3 \longrightarrow 2CH_4 + CH{\equiv}CH + H_2$$

3. These reactions occur whether the hydrocarbon is in contact with hydrogen or with other hydrocarbons.

Based as it was on the detailed work with the aliphatic hydrocarbons containing but one and two carbon atoms, it is not surprising that the theory met with later criticism. Bone, and particularly Haber, attacked Berthelot's views rather severely. Haber [11] pointed out that Berthelot's first proposal is but an arbitrary interpretation of the observation that in the gasification of hydrocarbons at progressively high temperatures, graphite always appears, noting however that coke is never free from hydrogen. With regard to the second of Berthelot's statements, Haber criticized it on the ground that an equilibrium indicates a permanent state eventually reached because of a permanent set of external conditions. The effect of temperature on the equilibrium is obscure, and furthermore, Berthelot's "methane equilibrium" is apparently incompatible with the irreversible formation of benzene from acetylene. Haber also noted the fact that aliphatic hydrocarbons with one or two carbon atoms constitute an isolated special case, somewhat different from their higher homologs. Berthelot particularly emphasized the importance of acetylene as a factor in the building-up processes. Although it is true that benzene may be prepared by the action of heat on acetylene, Bone has quite conclusively demonstrated the relative insignificance of acetylene as a product of pyrolysis of the simple hydrocarbons.

Nef's Theory

Nef was the champion of dissociation as the ultimate answer to the question of reaction mechanism. In his system, the original compound was always considered to dissociate into an ephemeral molecule of

bivalent carbon, which might then react with itself or with other neighboring substances. Thus:

$$\begin{matrix} a \\ b \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} x \\ y \end{matrix} \longrightarrow \left[\begin{matrix} a \\ b \end{matrix}\!\!>\!C\!<\right] + xy.$$

Nef's experiments were by no means limited to the field of pyrolysis, but these are the only ones which concern us here. A few cases will be selected to display his method of reasoning. When diphenylbromomethane is pyrolyzed (p. 137), very good yields of tetraphenyl ethylene result. According to Nef, therefore,

$$(C_6H_5)_2C\!<\!\!\begin{matrix} H \\ Br \end{matrix} \longrightarrow HBr + [(C_6H_5)_2C] \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2$$

Benzohydrol (p. 160) might be expected to give tetraphenyl ethylene also, but this is not the case. Instead, tetraphenylethane, benzophenone and diphenylmethane are the products of the reaction. Thus, Nef postulated the existence of diphenylmethylene as before, but the radical at once was considered to enter into reaction with water:

$$(C_6H_5)_2CHOH \longrightarrow H_2O + [(C_6H_5)_2C]$$

Then,

$$[(C_6H_5)_2C] + H_2O \longrightarrow (C_6H_5)_2CO + 2H,$$

and

$$[(C_6H_5)_2C] + 2H \longrightarrow (C_6H_5)_2CH_2,$$

or

$$2[(C_6H_5)_2C] + 2H \longrightarrow (C_6H_5)_2CH{-}CH(C_6H_5)_2.$$

This device, namely, the use of water in the elucidation of a reaction mechanism was frequently employed by Nef, but at present, because of its arbitrary nature, it is regarded with disfavor. For example, it is much more direct to consider that benzophenone is formed directly from the alcohol by dehydrogenation. In fact, hydrogen is actually an important product of the reaction, and with Nef's mechanism it is difficult to see why this should be true without the accompanying formation of oxygen. If water is the source of one it should also be the source of the other, but no trace of oxygen is liberated in the pyrolysis of benzohydrol.

Nef's experiments with ethyl chloride are particularly well adapted to show his method of reasoning. If ethyl chloride is first pyrolyzed in an empty tube (500-600°) and then passed through a soda-lime tube at 400°, the chief gaseous products[16] are water (from HCl on the soda-lime) and ethylene. If, however, the ethyl chloride is passed directly into a soda-lime tube at 350°, the gaseous products are hydro-

[16] Nef, *Ann.* 318, 14 (1901).

gen, methane, ethanol, some unchanged ethyl chloride and a very little ethylene. In the first case, Nef reasoned that ethylidene, $[CH_3—CH<]$, was formed which rearranged rapidly into ethylene. Since ethylene is inert towards water, it fails to react further and is isolated as such. In the second case, the methylmethylene is in immediate contact with the water, and so reacts prior to any rearrangement. Thus, ethyl alcohol as a product is explained.

To explain the formation of propionaldehyde from propylene glycol (p. 177), Nef postulated dehydration to the bivalent carbon residue, $\left[\begin{smallmatrix} CH_3—C—CH_2OH \\ \diagup\!\diagdown \end{smallmatrix}\right]$, which then would rearrange into the aldehyde, $CH_3—CH_2—CHO$. Trimethylene glycol (p. 180) pyrolyzes chiefly into acrolein, allyl alcohol and *n*-propyl alcohol, and Nef's conception of the equations involved follows. As before, there is a methylene dissociation and a subsequent reaction with water.

$$CH_2OH—CH_2—CH_2OH \longrightarrow [CH_2OH—CH_2—CH=] + H_2O$$

$$[CH_2OH—CH_2—CH—] \longrightarrow CH_2OH—CH=CH_2$$

and

$$[CH_2OH—CH_2—CH=] + H_2O \longrightarrow [CH_2OH—CH_2—CHO] + 2H$$

$$[CH_2OH—CH_2—CHO] \longrightarrow H_2O + CH_2=CH—CHO.$$

Then,

$$CH_2=CH—CH_2OH + 2H \longrightarrow CH_3—CH_2—CH_2OH.$$

A much simpler reaction mechanism is to consider an initial change of trimethylene glycol into allyl alcohol:

$$CH_2—CH—CH_2OH \longrightarrow CH_2=CH—CH_2OH + H_2O.$$

(OH H)

Then the allyl alcohol may become dehydrogenated in part to acrolein—a reaction which is known to occur (p. 157)—and the hydrogen which is liberated may reduce part of the allyl alcohol to propyl alcohol.

Nef's treatment of the pyrolysis of acetaldehyde and acetone is perhaps the most fanciful of any of his speculations. Acetaldehyde (p. 236) merely breaks into carbon monoxide and methane, and a complicated mechanism for this decomposition seems scarcely justified. Yet Nef postulated a methylene dissociation, as follows:

$$CH_3—CHO \longrightarrow [CH_2<] + [CH_2O] \longrightarrow [CH_2<] + [2H] + CO$$

$$[CH_2=] + 2H \longrightarrow CH_4$$

With acetone (p. 249), Nef assumed a primary dissociation into methylene and acetaldehyde to explain the observed production of methane,

ethylene and carbon monoxide. In the light of more recent investigations, this position becomes absolutely untenable, since the products are now known to be methane and ketene:

$$(CH_3)_2CO \longrightarrow CH_4 + CH_2{=}CO$$

Wieland's Rule.

A considerable amount of work on free radicals has been done by Wieland,[17] and a generalization concerning the decomposition of these radicals has been formulated by him. Essentially, the rule postulates disproportionation when a radical is decomposed by heat. If the free radical is ZH, H being a hydrogen atom and Z the remainder of the radical, then:

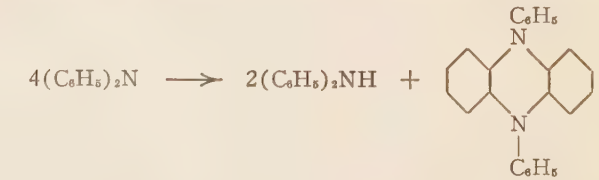
$$4ZH \longrightarrow 2ZH_2 + Z{=}Z.$$

A simple case illustrative of this rule, though it is not usually considered a thermal decomposition, is the decomposition of the hydroxyl group at the anode during electrolysis:

$$4OH \longrightarrow 2OH_2 + O{=}O.$$

Similarly, the decomposition of hydrogen peroxide into water and oxygen may be viewed by this mechanism if two hydroxyl groups are first formed.

Wieland has shown that at temperatures above 90°, tetraphenyl hydrazine exists as the radical diphenyl nitrogen. If this is boiled 30 minutes in a toluene solution there is formed a mixture of diphenylamine and diphenyl-dihydrophenazine. In this case the reaction is:



By rearrangement, there is also formed an isomer of tetraphenyl hydrazine, namely, *o*-anilinotriphenylamine, $C_6H_5NH{-}C_6H_4{-}N(C_6H_5)_2$.

Goldschmidt [18] has made interesting applications of Wieland's rule. In the oxidation of aniline, there is formed the radical, $C_6H_5NH{-}$, which, if not removed by such an agency as triphenylmethyl, decomposes as follows:

$$2C_6H_5NH \longrightarrow C_6H_5NH_2 + (C_6H_5{-}N{=})_x.$$

The $(C_6H_5{-}N{=})_x$ represents either azobenzene, or *N*-phenyl-quinone-

[17] Wieland, *Ann.* **381**, 202 (1911).
[18] Goldschmidt and Wurzschnitt, *Ber.* **55**, 3216 (1922).

diimide, $C_6H_5—N=C_6H_4=NH$. A similar case [19] in which triphenylmethyl acts as a hydrogen acceptor may be noticed in the decomposition of hydrazobenzene. If these two substances are heated for five hours, triphenylmethane and azobenzene are formed:

$$2(C_6H_5)_3C + C_6H_5—NH—NH—C_6H_5 \longrightarrow 2(C_6H_5)_3CH + C_6H_5N=NC_6H_5.$$

Unstable Groupings.

There are certain groups which possess great instability. In many cases this instability is of such an order that the desired compounds cannot be isolated. Essentially, their decomposition into the more stable compounds are pyrolyses, even though the temperature of the conversion is comparatively low. Some of these unstable configurations are:

$$=C(OH)_2,\ —C(OH)_3,\ HO—\overset{\diagup\diagdown}{C}—OR,\ HO—\overset{\diagup\diagdown}{C}—Cl,\ HO—\overset{\diagup\diagdown}{C}—NH_2,$$

$$=C(NH_2)_2,\ =C(NHOH)_2, \text{ and } =C(CO_2H)_2.$$

A rough attempt at a classification, with the terminology taken from "color and constitution," has been made by Herzog.[20] He noted that certain compounds which possess a tendency to resinify when heated above their melting points contain the "resinophore groups":

$$—N=C=N—,\ —N=\underset{|}{P}=N—,\ =C=\underset{|}{C}—CO—, \text{ or } —C=C—C=C—.$$

An "auxoresinous" group is —C=C— in —C=C—CO—C=C—.

The Methane System of Compounds.

One of the very few reactions of the paraffins is that of pyrolysis. Alcohols have several type reactions, as do aldehydes and acids, but the one reaction which they have in common with hydrocarbons is that of pyrolysis. Therefore, to draw an analogy between hydrocarbons and other homologous series, it is suggested that there may be a "methane system" which is comparable to the "water system" or to the "ammonia [21] system". Just as the hydroxyl group is related to water, and the amino group to ammonia, so the methyl group is related to methane.

Water System	*Ammonia System*	*Methane System*
$H—O—H$	$H—NH_2$	$H—CH_3$
$R—O—H$	$R—NH_2$	$R—CH_3$
$R_2C=O$	$R_2C=NH$	$R_2C=CH_2$, etc.

The similarity in the thermal decomposition of these related compounds appears even in the simplest members. Water, ammonia and

[19] Goldschmidt, *Ber.* **53**, 28 (1920).
[20] Herzog, *Tech. Ind. Schweiz. Chem. Ztg.* **1923**, 84; *Chem. Abstracts* **18**, 3372 (1924); *Oesterr. Chem. Ztg.* **29**, 216 (1926); *Chem. Abstracts* **21**, 1463 (1927).
[21] See especially the work of E. C. Franklin.

methane, in comparison with other compounds in their respective systems, are very resistant to heat, and furthermore all three substances change directly into their constituent elements on decomposition. This similarity extends to more complicated members of the respective systems, and, by analogy with the pyrolysis of members of the water system, it is frequently possible [22] to predict in a qualitative way the course of pyrolysis in the methane system.

ALCOHOLS.

The simplest alcohol of the water system, namely, methanol, may be regarded as a substituted methane, in which one hydrogen has been replaced by hydroxyl. The simplest "alcohol of the methane system" is ethane, since a hydrogen in methane has been replaced by methyl. Methanol pyrolyzes with the elimination of water, and also with the elimination of hydrogen. Ethane also decomposes in two ways, with the elimination of methane and of hydrogen.

Ethane					*Methanol*				
$CH_3—CH_3$	$\longrightarrow$	CH_4	+	$[CH_2]$	CH_3OH	$\longrightarrow$	H_2O	+	$[CH_2]$
or	$\longrightarrow$	H_2	+	C_2H_4	or	$\longrightarrow$	H_2	+	HCHO

Propane and ethanol are comparable, and in general the following reactions may be considered as representative of the initial stages of the thermal decomposition:

$$R—CH_2—CH_2—CH_3 \begin{cases} \longrightarrow CH_4 + R—CH=CH_2 \\ \longrightarrow H_2 + R—CH_2—CH=CH_2 \end{cases}$$

$$R—CH_2—CH_2OH \begin{cases} \longrightarrow H_2O + R—CH=CH_2 \\ \longrightarrow H_2 + R—CH_2—CH=O \end{cases}$$

It must not be thought that the location of scission in hydrocarbons is always at the terminal carbon atom, because, on the same type of argument, there may be an ethane system or a propane system also. In other words, ethane may be eliminated in some cases in place of methane, etc. The position of scission may be determined by the relative electron attraction of the radicals which will be discussed directly.

Tertiary butyl alcohol and tetramethylmethane would be analogous compounds in the two systems. The former is known to pyrolyze almost exclusively into *iso*butylene and water, and it is reasonable to infer that tetramethylmethane would decompose into *iso*butylene and methane. It is interesting to point out that the following groupings are com-

[22] Presented by the author at the fall meeting of the American Chemical Society, Philadelphia, 1926.

parable: $=C(OH)_2$ and $=C(CH_3)_2$. The former is known to be very unstable; the idea that the latter may be an unstable one at elevated temperatures is supported by the little evidence which is available. To cite but one instance, methane has been found to be a major product of decomposition of *iso*pentane, whereas it plays a minor rôle in the decomposition of *n*-pentane (p. 70).

ETHERS.

Saturated aliphatic ethers decompose according to the following general equation:

$$RCH_2—O—CH_2R \longrightarrow R—CH_3 + O{=}CHR.$$

The comparable reaction in the methane system of compounds is:

$$RCH_2—CH_2—CH_2R \longrightarrow R—CH_3 + H_2C{=}CHR.$$

This type of pyrolysis is well known; it is the recognized equation for the cracking process. This equation supplements the alternative equation for straight chain hydrocarbons, in which methane is eliminated from the terminal position. Thus, *n*-pentane has been found to decompose between carbon atoms 2,3 as well as between 1,2. Other straight chain hydrocarbons behave similarly.

ALDEHYDES.

Ethylene is the "formaldehyde of the methane system" since it is derivable either from ethane (the alcohol) with the loss of 2 hydrogens, or from methane by substitution of 2 methyls followed by the elimination of CH_4 (comparable to the substitution of 2 hydroxyls followed by the elimination of H_2O). The decomposition of ethylene is certainly more involved than is that of formaldehyde, but the primary decomposition in both is the detachment of a molecule of hydrogen:

$$H_2C{=}CH_2 \longrightarrow H_2 + HC{\equiv}CH$$

and

$$H_2CO \longrightarrow H_2 + CO.$$

In general, monosubstituted olefines, $R—CH{=}CH_2$, may be regarded as methano-aldehydes. Thus, propylene may decompose in part into methane and acetylene, simulating the decomposition of acetaldehyde into methane and carbon monoxide. However, as will be shown later, acetylenes are never formed from higher hydrocarbons except in traces, at temperatures up to 600°.

This hypothesis infers that the scission of an olefine by thermal means occurs at the single bond in preference to the double bond. The limited number of pure olefines which have been pyrogenically decom-

posed lends confirmatory evidence to this view. However, it is unsafe to predict that acetylene should always be a product, since higher olefines may undergo scission between the singly linked carbon atoms wherever they occur in the molecule.

Another point which is obvious from the above discussion is the fact that acetylene is the "carbon monoxide of the methane system". The similarity of acetylene to carbon monoxide has been previously recognized. Lewis[22a] ascribes the following formulas to them, H:C:::C:H and :C:::O:. Prussic acid is formulated similarly, and it is obvious that prussic acid is the "carbon monoxide of the ammonia system". Its formation from the ammono-alcohol, methylamine, by the loss of 4 hydrogens is comparable to the relationship of CH_3OH to CO, or of C_2H_6 to C_2H_2. This analogy is further borne out by the fact that formic acid, formamidine and propylene, which are respectively the simplest aquo, ammono and methano acids, differ from their respective "carbon monoxide" by the elements of water, ammonia and of methane.

Acids.

Formic acid is peculiar in that it possesses an aldehyde group as well as a carboxyl group. This is reflected in its pyrolysis:

$$H{-}CO{-}OH \begin{cases} \nearrow & H_2O + CO \quad \text{(as an aldehyde)} \\ \searrow & H_2 + CO_2 \quad \text{(as an acid)} \end{cases}$$

Propylene, which has already been mentioned as a methano-aldehyde, is also a methano-acid, the analog of formic acid. Thus, the following two types of decomposition might be predicted:

$$H{-}C \begin{cases} = CH_2 & \nearrow \\ & \searrow \\ - CH_3 & \end{cases} \begin{matrix} CH_4 + C_2H_2 \quad \text{(as an aldehyde)} \\ \\ H_2 + CH_2{=}C{=}CH_2 \quad \text{(as an acid)} \end{matrix}$$

*Iso*butylene is the analog of acetic acid. In general, $R{-}C(CH_3)_2{-}CH_2$ represents a methano-acid.

The course of the pyrolysis of acetic acid may be explained on the basis of two concurrent reactions:

$$CH_3{-}CO_2H \longrightarrow CH_4 + O{=}C{=}O,$$

and

$$CH_3{-}CO_2H \longrightarrow H_2O + CH_2{=}C{=}O.$$

[22a] G. N. Lewis, Valence and the Structure of Atoms and Molecules, (Chemical) Catalog Co., 1923, p. 127.

The first of these two reactions has long been accepted, and the second has recently been established (p. 334) in the author's laboratory.[23]

These two reactions merge into one when the analogous case in the methane system is considered. *Iso*butylene should pyrolyze into methane and allene (or its decomposition products):

$$(CH_3)_2C{=}CH_2 \longrightarrow CH_4 + CH_2{=}C{=}CH_2.$$

At present, this is only conjecture for *iso*butylene has not been studied in this connection. Carbonic acid, acetic acid, acetone and *iso*butylene have never been regarded as members of a series in the ordinary reactions of organic chemistry, yet each one differs from the next by a methyl group in place of hydroxyl, or by methylene in place of carbonyl-oxygen. Carbonic acid is a true aquo-acid, and *iso*butylene is a true methano-acid; acetic acid and acetone are mixed aquo and methano acids. The course of the pyrolyses of carbonic acid, acetic acid and acetone are in striking agreement with each other; *iso*butylene should decompose similarly.

$$\begin{aligned} HO{-}CO{-}OH &\longrightarrow H_2O + O{=}C{=}O \\ CH_3{-}CO{-}OH &\longrightarrow CH_4 + O{=}C{=}O \\ CH_3{-}CO{-}CH_3 &\longrightarrow CH_4 + CH_2{=}C{=}O \\ CH_3{-}C(CH_3){-}CH_3 &\longrightarrow CH_4 + CH_2{=}C{=}CH_2 \end{aligned}$$

The thermal decomposition of urea into ammonia and *iso*cyanic acid and the decomposition of triphenyl guanidine into aniline and carbodiphenylimide emphasize the same relationships in the ammonia system:

$$C_6H_5NH{-}C(NC_6H_5){-}NHC_6H_5 \longrightarrow C_6H_5NH_2 + C_6H_5N{=}C{=}NC_6H_5.$$

Thus, whereas it has long been recognized that *iso*cyanates and ketenes have much in common, it is now pointed out that they are members of the series which starts with carbon dioxide and ends with allene.

Esters.

Methyl formate and butene-1 are comparable. Butene has already been mentioned as a "methano-aldehyde". Methyl formate also possesses an aldehyde grouping; it decomposes thermally into formaldehyde:

$$HCO_2CH_3 \longrightarrow 2HCHO.$$

If the decomposition of butene parallels that of methyl formate, it should decompose into 2 molecules of ethylene. As an "aldehyde", butene would pyrolyze into ethane and acetylene. Higher esters, $R{-}CO{-}O{-}CH_2{-}CH_2R'$, decompose quite characteristically into an

[23] Hurd and Martin, unpublished results.

From a consideration of the order "phenyl > methyl > ethyl > benzyl", it is obvious that scission by the first reaction should predominate and this seems to be the case.

Dibenzyl.

There are also two possible modes with dibenzyl:

(1) $C_6H_5—CH_2—CH_2—C_6H_5 \longrightarrow 2[C_6H_5—CH_2—]$,

or

(2) $C_6H_5—CH_2—CH_2—C_6H_5 \longrightarrow [C_6H_5—] + [—CH_2CH_2—C_6H_5]$.

The benzyl radical has far less electron attraction than the phenyl, and presumably also less than the phenylethyl. Therefore, the first reaction would be anticipated. As will be shown in more detail later, dibenzyl changes into toluene and stilbene. Thus (compare Wieland's rule, p. 20):

$$4[C_6H_5CH_2—] \longrightarrow 2C_6H_5CH_3 + 2[C_6H_5CH=]$$
$$2[C_6H_5CH=] \longrightarrow C_6H_5CH=CHC_6H_5$$

Hexaphenyl Ethane.

As is well known, hexaphenyl ethane dissociates into triphenylmethyl. The alternative dissociation into phenyl and pentaphenylethyl has never been noticed, nor would it be expected from this viewpoint. Phenyl exerts a strong pull on its valence electrons, and triphenylmethyl a very weak pull (see p. 745).

Hexamethyl Ethane.

Hexamethyl ethane also offers two possibilities for dissociation, namely, into two tertiary butyl radicals or into a methyl and a pentamethylethyl radical. Methyl certainly possesses the most electron attraction of the three and this should tend to prevent its appearance. If the former is the exclusive type, then either *iso*butylene and *iso*butane or their decomposition products might be expected. Actually (p. 73), there seems to be evidence for methane, propylene and *iso*butylene. *Iso*butane is known to undergo pyrolysis into methane and propylene (p. 66). This would seem to be very good confirmatory evidence for the above method of reasoning. However, it is possible that the two tertiary butyl radicals react with each other by a kind of disproportionation, and that the actual transitory formation of *iso*butane may never occur. In this case, and this is true in other illustrations as well, the "nascent paraffin" is quite decomposed at a temperature which is usually not very injurious to the pure paraffin. Thus, methane appears

to be the only paraffin in the gas from hexamethyl ethane at 550-570°, whereas *iso*butane is known to be fairly stable at that temperature (only about half of the *iso*butane is decomposed in ten minutes at 650°) if the time of exposure is limited. Thus, instead of the reaction,

$$2[(CH_3)_3C—] \longrightarrow (CH_3)_3CH + (CH_3)_2C{=}CH_2$$

the following may be nearer the truth:

$$[(CH_3)_2C(CH_3)] + [H—]CH_2C(CH_3)_2] \longrightarrow CH_4 + (CH_3)_2C{=}CH_2 + [(CH_3)_2C{=}]$$

$$[(CH_3)_2C{=}] \longrightarrow CH_2{=}CH{=}CH_2$$

The author is indebted to Professor James B. Conant for suggesting the latter equation.

Concerning unsaturated hydrocarbons, see p. 76.

The Electron Attraction of the Hydrogen Radical.

Lucas' interpretation of the fact that benzoic acid has a greater ionization constant than *p*-toluic acid (p. 27) is that the *p*-H radical has a greater electron attraction than the *p*-CH_3 radical. Since the methyl radical, in turn, appears to have a greater electron attraction than other alkyl groups, it follows that the hydrogen radical exerts more electron attraction than alkyl groups (see p. 127). Skraup and Freundlich (p. 37), by the method of halochromy, have reached an apparently opposite conclusion, but too much emphasis should not be given to a literal interpretation of their data. Instead, the data show that the values of H—, CH_3— and C_2H_5— are of much the same order of magnitude and that these values are considerably below the value for aryl radicals.

So also, Levy and Sfiras [30] have established that the radicals, $C_6H_5—(CH_2)_{1\text{ to }4}—$, have less electron attraction than hydrogen, since the rearrangement of the ethylene oxide derivatives, $C_6H_5—(CH_2)_x—CH—CH_2$ (O), ($x = 1$ to 4) yields ketones, $C_6H_5—(CH_2)_x—CO—CH_3$, and not aldehydes. The argument is advanced that the carbon-to-oxygen bond is severed, giving $C_6H_5—(CH_2)_x—CH(O)—CH_2$ momentarily, on the side nearer to the radicals with greater electron attraction.

Baudisch and Davidson have likewise found [31] that the rate of

[30] Levy and Sfiras, *Compt. rend.* **184**, 1335 (1927); *see also* this monograph, pp. 38, 183.
[31] Baudisch and Davidson, *J. Biol. Chem.* **75**, 247 (1927).

catalyzed oxidation of 5-substituted hydantoins, $\begin{matrix} NH—CO—NH \\ | \quad\quad\quad | \\ CHR———CO \end{matrix}$, is a function of the nature of the substituting (R) group. If these groups are arranged in descending order of their enhancing action on the oxidation rate, the sequence is: phenyl > hydrogen > methyl > benzyl.

As regards aliphatic hydrocarbons, Pease [31a] states that there is evidence based on thermal data that the energy required for complete destruction of a C—C linkage is about 72,000 calories per mol, and for a C—H linkage about 92,000 calories per mol. These are not rigid values, since there are minor variations in the energies of the C—C and the C—H linkages in different hydrocarbons.

The data on the pyrolysis of hydrocarbons may be readily interpreted by considering that the electron attraction of the hydrogen radical is, in general, lower than aryl and higher than alkyl radicals; thus, Ar > H > R. Cracking processes (aliphatic), which are so familiar, are dependent on C—C scission rather than C—H scission. This is emphasized in Haber's rule. Actually, both types of scission are met in practice. At sufficiently high temperatures, hydrogen is always encountered, but this is usually above 600°, whereas cracking operations may proceed at lower temperatures. At higher temperatures other factors must appear inasmuch as hydrogen is formed. A few examples of hydrogen elimination from hydrocarbons will be listed.

Methane. Little if any effect by heat alone, in the absence of catalysts, is apparent below 800°. Between 800-1200° the sole effect is a decomposition into the elements. Traces of ethane and acetylene, at the temperatures of the electric arc, bear witness to the dissociation into the radicals [CH_3—] and [HC≡], but in the main, all four hydrogens of methane are equally eliminated.

Ethane. Carbon and hydrogen are formed at lower temperatures from ethane than from methane. Carbon is produced in quantity, as is ethylene. The progress of the reaction, insofar as hydrogen evolution is concerned, may be represented by the following equation:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \rightleftharpoons C_2H_2 + 2H_2 \longrightarrow 2C + 3H_2.$$

Propane. The fact that propane contains hydrogen atoms attached to secondary as well as to primary carbon atoms means that one type of hydrogen is more electronegative than the other (p. 27). This may be instrumental in causing the elimination of two neighboring hydrogen atoms as molecular hydrogen.

[31a] Pease, *J. Am. Chem. Soc.* **50**, 1784 (1928).

Benzene. Pyrolysis does not rupture the benzene nucleus unless the temperature is particularly high. Therefore, there is but one mode of scission into radicals:

$$C_6H_6 \longrightarrow [C_6H_5—] + [H—].$$

To be sure, these radicals may recombine and undoubtedly they do, but at the high temperature of the reaction—a temperature which would also cause hydrogen evolution in aliphatic compounds—this is largely prevented. Thus the radicals may unite with other like radicals to form molecular hydrogen and biphenyl.

The fact that the actual existence of the simple alkyl radicals has not been demonstrated may be cited by some as an objectionable feature of this theory. However, the evidence conforms excellently with the theory in the known cases wherein the existence of radicals has been demonstrated, namely, in the dissociation of the hexaaryl ethanes. The mere fact that methyl, or benzyl, or other radicals have not been isolated should not weigh heavily against a theory which is otherwise useful. In fact, Gomberg [31b] has recently stated that it is becoming more and more customary to interpret the mechanism of many reactions, not necessarily reactions of pyrolysis, by assuming that the reacting molecules first split into the respective radicals later to unite and form new molecules. A somewhat different theory to explain the results from the pyrolysis of methane, ethane, ethylene and acetylene has been developed by Bone and Coward, and will be considered later when these hydrocarbons are discussed in detail.

One difficulty with the theory of electron attraction, and one which has no adequate explanation at present, is the fact that the order of electron attraction of radicals varies somewhat depending on the method which is used in its determination. Tiffeneau [32] has given a summary of various attempts to establish this order of "affinity capacity". The methods used are both direct and indirect. In the direct methods, the radical in question is severed from the molecule and the final products of the reaction are sought as the working basis. In the indirect methods, the radical in question influences the rupture of some other part of the molecule, but does not become severed itself. These results may be interpreted either by a study of the final products, or by the velocity of the reaction, or by the equilibrium state. General equations may be used to represent the direct and indirect methods:

Direct: $R—A—R' \longrightarrow [R—] + [—AR']$, or $[RA—] + [—R']$
Indirect: $R—C—A—C—R' \longrightarrow [RCA—] + [—CR']$, or $[RC—] + [—ACR']$.

[31b] Gomberg, *Ind. Eng. Chem.* **20**, 159 (1928).
[32] Tiffeneau and Orekhoff, *Inst. Intern. Chim. Solvay, 2ième Cons. Chim.* **1926**, 247-321.

Direct Methods of Determining the Order of Electron Attraction.

As an illustration of the latter assume the compound, $RCH(X)—CHR'(X)$, is to be ruptured between C and X. Then R and R′ will influence the particular X which is lost. Another indirect mechanism is to cause the rupture between A and X in the series R—A—X, R′—A—X, R″—A—X, etc. Then, R, R′ and R″ may be compared.

Kharasch's method, which has been given, is a direct method. Others follow.

(a) *Double Decomposition of Unsymmetrical Ketones by Sodamide.*[33] This is a pyrolytic method (see p. 269):

$$\mathrm{Ar}\diagdown\!\!\diagup\mathrm{C}\!<\!\!\begin{matrix}\mathrm{ONa}\\ \mathrm{NH_2}\end{matrix}\ \xrightarrow{\text{heat}}\ \mathrm{ArH} + \mathrm{Ar'—CO—NHNa}.$$

This method has only been applied for aryl radicals. Without going into details, the following order has been established:

p-anisyl > β-naphthyl > xenyl (*p*-diphenyl) > phenyl > *p*-chlorophenyl > *p*-bromophenyl > *m*-chlorophenyl > *m*-bromophenyl.

(b) *Action of Cyanogen Bromide*[34] *on Amines, Arsines and Sulfides.* In this case,

$$\mathrm{R_3N} + \mathrm{CNBr} \longrightarrow \mathrm{R_3N}\!<\!\!\begin{matrix}\mathrm{CN}\\ \mathrm{Br}\end{matrix}.$$

If this compound is heated lightly it pyrolyzes according to the following equation:

$$\mathrm{R'—N(R)(R'')(CN)(Br)} \longrightarrow \mathrm{RBr} + \mathrm{R'R''N—CN}.$$

The following order results from these experiments:

phenyl > butyl > propyl > ethyl > methyl > benzyl > allyl > crotyl.

In this series, phenyl has the largest "affinity capacity", or is the most electronegative. In other words, it is most firmly tied by its valence bond. The same order is established by heating the arsine derivative:

$$\mathrm{R_3As(CN)Br} \longrightarrow \mathrm{R_3AsCN} + \mathrm{RBr},$$

[33] Schönberg, *Ann.* **436**, 205 (1924); *Ber.* **58**, 580 (1925).
[34] von Braun and Moldaenke, *Ber.* **56**, 2165 (1923); von Braun and Engel, *Ann.* **436**, 299 (1924); Steinkopf, *Ber.* **55**, 2597 (1922).

or by heating the sulfide derivative:

$$R_2S(CN)Br \longrightarrow R{-}S{-}CN + RBr.$$

However, in the latter case, the positions of benzyl and allyl are reversed. Finally, from the following pyrolysis:

$$C_6H_5{-}CCl_2{-}N(R)(R') \longrightarrow R'Cl + C_6H_5CCl{=}NR,$$

the same order results which was observed with amines. By the action of cyanogen bromide on tertiary amines, von Braun has also determined the following series:

methyl > β-naphthylmethyl > α-naphthylmethyl > benzyl > p-methylbenzyl > p-ethylbenzyl > p-phenylbenzyl.

(c) *Action of Metallic Sodium on Ethers.*[35]

$$R{-}O{-}R' + 2Na \longrightarrow RONa + R'{-}Na.$$

This reaction gives:

phenyl > naphthyl (α or β) > pentyl > ethyl > benzyl.

Most other methods reverse the relative positions of naphthyl and phenyl.

INDIRECT METHODS.

(a) MEASURE OF REACTION VELOCITY.

1. *Speed of Reduction*[36] *of Substituted Phenylhydrazines.*

$$Ar{-}NH{-}NH_2 + 2H \text{ (from } SnCl_2 + HCl) \longrightarrow ArNH_2 + NH_3$$

By this method the following order is obtained:

2,6-dimethylphenyl (220.5) > 2,4,6-trimethylphenyl (210) > 2,4-dimethylphenyl (131) > o-tolyl (2.9) > o-iodophenyl > p-iodophenyl > p-tolyl (2.3) > m-tolyl (1.1) > p-chlorophenyl > p-bromophenyl > m-iodophenyl > m-bromophenyl > m-chlorophenyl > p-carboxyphenyl (0.5).

The values in parentheses give the relative quantitative values on the basis of phenyl = 1.

2. *Velocity Constants*[37] *of the Reactions between the Alcohols and p-Nitrobenzoyl Chloride, and the Temperature of the Ethers, $R{-}O{-}C(C_6H_5)_3$, wherein R is the Alkyl Group in the Aforementioned Alcohols.* The velocity constants with the various alcohols are as fol-

[35] Schorigin, *Ber.* 57, 1627 (1924).
[36] Franzen, *J. prakt. Chem.* [2] 97, 61, 446 (1918).
[37] Norris and Young; presented by Professor Norris at the Organic Symposium, Columbus, Ohio, December, 1927.

lows: methyl 0.184; ethyl 0.085; *n*-butyl 0.074; *iso*amyl 0.073; *n*-propyl 0.066; *iso*butyl 0.031; secondary propyl 0.010; secondary butyl 0.0074; secondary amyl (pentanol-2) 0.0059. It is apparent that the primary radicals all have bigger values than the secondary radicals. A striking feature is that the same order exists for the temperature of decomposition of the corresponding alkyl triphenylmethyl ethers.

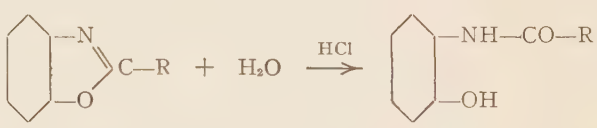
The temperature of decomposition for various alkyl groups in these ethers is: methyl 281°; ethyl 257°; *n*-butyl 254°; *iso*amyl 251°; *n*-propyl 244°; *iso*butyl 239°; secondary propyl 234°; secondary butyl 222°; secondary amyl 233°. Only in this last case, is the order different from the order obtained by velocity constants. The general reaction for the pyrolysis of these ethers leads to the formation of triphenyl methane and the corresponding aldehyde or ketone:

$$(C_6H_5)_3C{-}O{-}CHR_2 \longrightarrow (C_6H_5)_3C{-}H + O{=}CR_2.$$

The sequence of radicals from this work is:

methyl > ethyl > *n*-butyl > *iso*amyl > *n*-propyl > *iso*butyl > secondary propyl > secondary butyl or secondary amyl.

3. *Conversion of 2-Alkyl (or Aryl) Benzoxazoles into ortho-Acyl Aminophenols.*[38] Depending on the group R in the equation:



quite different speeds of reaction are realized. Thus, a 50 percent conversion with a benzyl substituent is realized in 35 minutes, whereas a similar conversion with *n*-hexyl occurs in 3 hours; with methyl in 40 hours; with phenyl in 74 hours; and with *p*-tolyl, naphthyl or *p*-anisyl in 120 hours. From such data, it is established that

α-naphthyl > β-naphthyl > *p*-anisyl > phenyl > methyl > tertiary butyl > *iso*butyl > cyclohexyl > *n*-hexyl > benzyl.

The tertiary butyl group appears to occupy an anomalous position.

4. *Metathesis*[39] *of Substituted Benzyl Chlorides with Sodium Ethylate.* The velocity depends on the aryl substituent, but there are too few results as yet to make the method one of real value.

$$ArCH_2Cl + C_2H_5ONa \longrightarrow NaCl + ArCH_2{-}O{-}C_2H_5.$$

This reaction appears to establish the series:

p-xenyl > *o*-tolyl > *p*-ethylphenyl > *p*-tolyl > *m*-tolyl > phenyl.

[38] Skraup, *Ann.* **419**, 1 (1919); Skraup and Moser, *Ber.* **55**, 1080 (1922).
[39] Franzen, *J. prakt. Chem.* [2] **97**, 61 (1918); von Braun and Engel, *Ann.* **436**, 319 (1924).

(b) Methods Based on a Study of the Equilibrium State.

(1) *Dissociation of Hexaarylethane into Triarylmethyl.*[40] This dissociation depends not only on the nature of the aryl radical, but also on the temperature and the nature of the solvent. Since this is an indirect method, it should be emphasized that the method seeks to establish the order of negativity of various aryl radicals, not of the triarylmethyl radicals. The method is obviously of value only with aryl radicals (those which are highly electronegative), and in cases where 100 percent dissociation is attained there can be no comparison. The negative nature of the xenyl group is apparent from the following series: $(C_6H_5)_3C$, $C_6H_5—C_6H_4—C(C_6H_5)_2$, $(C_6H_5—C_6H_4)_2C—C_6H_5$ and $(C_6H_5—C_6H_4)_3C$, in which the dissociation (in benzene) respectively is 3, 15, 80 and 100 percent. This series has been established:

$$\alpha\text{-naphthyl} > p\text{-anisyl} > p\text{-tolyl} > \text{phenyl}.$$

(2) *Halochromy;*[41] *the Decoloration of Triarylcarbinol "Sulfate" by the Addition of Alcohol.* The quantity of diluent needed depends on the groups present. Thus, in the case of $(C_6H_5)_2C<^{\text{Ar (or R)}}_{\text{OH}}$, this method indicates the series:

$$\underset{(17.74)}{p\text{-nitrophenyl}} > \text{naphthyl} > \underset{(6.99)}{p\text{-anisyl}} > \underset{(3.19)}{\text{xenyl}} > \underset{(2.55)}{p\text{-tolyl}} >$$

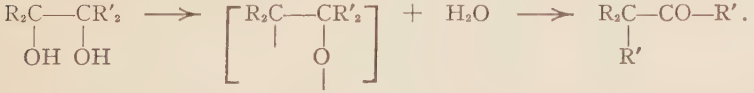
$$\underset{(1.08)}{p\text{-carboxyphenyl}} > \underset{(1)}{\text{phenyl}} > \underset{(0.56)}{m\text{-nitrophenyl}} > \underset{(0.360)}{\text{methyl}} > \underset{(0.343)}{\text{ethyl}} >$$

$$\underset{(0.330)}{\text{hydrogen radical}}.$$

The figures are merely comparative on the basis of phenyl as 1. The enormous exaltation of the *p*-nitro group in *p*-nitrophenyl is especially noteworthy. This is in decided contrast to the *m*-nitrophenyl group, which is the only aryl group lower than phenyl.

(c) Methods Based on an Investigation of the Final Products.

(1) *Dehydration of Bitertiary α-Glycols.*[42]



[40] Gomberg and Sullivan, *J. Am. Chem. Soc.* **44**, 1829 (1922); Gomberg and Forrester, *ibid.* **47**, 2373 (1925); and many other papers by Gomberg. *Also* Schlenk, Weichel and Herzenstein, *Ann.* **394**, 186 (1912); *Ber.* **43**, 1756 (1910); *Ann.* **372**, 4 (1909). *See also* Reference 32.

[41] Baeyer and Villiger, *Ber.* **35**, 3013 (1902); Kaufmann, *Ber.* **46**, 3788 (1913); **52**, 1422 (1919); Skraup and Freundlich, *Ber.* **55**, 1073 (1922); *Ann.* **431**, 243 (1923).

[42] Tiffeneau, *Compt. rend.* **143**, 687 (1906); *Ann. chim. phys.* [8] **10**, 330 (1907); *Rev. gen. sci.* **18**, 589 (1907). Meerwein, *Ann.* **396**, 200 (1913); **419**, 121 (1919). Orekhoff, *Bull. soc. chim.* **25**, 9 (1919). Nybergh, *Ber.* **55**, 1960 (1922). Tiffeneau and Levy, *Compt. rend.* **186**, 84 (1928).

In the dehydration of the pinacol, $\begin{matrix}(CH_3)_2C{-}C(C_2H_5)_2\\ \quad|\quad\quad|\\ \quad HO\quad OH\end{matrix}$, Meerwein established the fact that the ketones, $CH_3{-}CO{-}C(CH_3)(C_2H_5)_2$ and $C_2H_5{-}CO{-}C(CH_3)_2{-}C_2H_5$ were formed in a ratio of 1 : 20. Methyl, in other words, is more firmly tied by its valence electrons; thus, it has the larger affinity capacity. The series:

$$\textit{iso}\text{butyl} > \underset{(20)}{\text{methyl}} > \underset{(16)}{\text{propyl}} > \underset{(10)}{\text{butyl}} > \underset{(1)}{\text{ethyl}} > \textit{iso}\text{propyl} > \text{benzyl}$$

was obtained in this manner. It differs from the results of other methods.

(2) *Isomerization of Ethylene Oxides*[43] *by Heat.* Here again, an order of decreasing affinity capacities has been established:

$$\text{anisyl} > \text{phenyl} > \text{methyl} > \text{hydrogen radical.}$$

The results in this case are somewhat more difficult to interpret, but in general hydrogen has a greater tendency to migrate than alkyl radicals, but there is no fixed rule when the phenyl and the hydrogen radicals are to be compared. General equations are

$$R{-}\underset{\diagdown\,\diagup\ O}{CH{-}CH_2} \longrightarrow RCH_2{-}CHO \quad ; \quad \underset{\diagdown\,\diagup\ O}{R_2C{-}CH_2} \longrightarrow R_2CH{-}CHO$$

According to Tiffeneau and Klages, the latter rearrangement is more facile than the former.

$$R{-}\underset{\diagdown\,\diagup\ O}{CH{-}CHR'} \longrightarrow RCH_2{-}CO{-}R'$$

$$Ar{-}\underset{\diagdown\,\diagup\ O}{CH{-}CR_2} \longrightarrow \left[\begin{matrix}Ar{-}CH{-}CR_2\\ \quad\quad|\quad\quad|\\ \quad\quad O\quad\quad|\\ \quad\quad|\end{matrix}\right] \longrightarrow \begin{matrix}H{-}CO{-}CR_2\\ \quad\quad\quad|\\ \quad\quad\quad Ar\end{matrix}$$

The foregoing discussion has emphasized the fact that different methods yield somewhat different results. This may be due in part to the fact that some methods depend upon reaction rates. For a good survey of *rates* as opposed to *equilibria,* see Adkins and Adams, *J. Am. Chem. Soc.* **47,** 1368 (1925). A summary of the results of various investigators follows:

Tiffeneau:	*iso*butyl > methyl > propyl > butyl > ethyl > *iso*propyl > benzyl.
Meerwein:	methyl > propyl > butyl > ethyl.
Skraup and Freundlich:	methyl > ethyl > hydrogen.
von Braun:	butyl > propyl > ethyl > methyl > benzyl > allyl.
Kharasch:	methyl > ethyl > propyl > butyl > *iso*amyl > benzyl > hexadecyl.
Norris:	methyl > ethyl > *n*-butyl > *iso*amyl > *n*-propyl > *iso*butyl > secondary propyl > secondary butyl or secondary amyl.
Schorigin:	pentyl > ethyl > benzyl.
Skraup:	methyl > tertiary butyl > *iso*butyl > *n*-hexyl > benzyl.
Lucas:	primary alkyl > secondary alkyl > tertiary alkyl (isomers).

[42] Tiffeneau and Levy, *Bull. soc. chim.* **39,** 763 (1926); for other references, see pp. 31, 183.

In spite of the anomalies, all the results save von Braun's indicate that methyl is more electronegative than other alkyl groups, and that allyl and benzyl are at the opposite end of the series. The pyrolytic rearrangements of the aryl allyl ethers into *o*-allyl phenols (see under ethers) is further evidence of the extremely labile nature of the allyl group. Another point of universal agreement is that aryl groups exert greater electron attraction than the methyl group. Furthermore, the evidence shows that the *p*-methyl, *p*-methoxy, *p*-iodo and especially *p*-nitro groups augment the electron attraction of the phenyl nucleus, whereas the *p*-chloro, *m*-halogeno, and particularly *m*-nitro groups lessen its electron attraction.

Other Applications of the Principle of Electron Attraction in Pyrolysis.

Throughout the monograph, opportunities will frequently present themselves to explain the results of pyrolyses in a series of related compounds from the standpoint of electron attraction. Some of these cases will be briefly mentioned.

The great electron attraction of the *p*-nitrophenyl radical displays itself in *p*-nitrophenyl-azo-triphenylmethyl (p. 636); it is more stable towards heat than other substances of the general formula, $Ar—N=N—C(C_6H_5)_3$.

The series "$CH_3 > C_6H_5CH_2 > (C_6H_5)_2CH > (C_6H_5)_3C$" manifests itself in the comparative ease of rearrangements of compounds in the hydroxamic acid series;[44] acethydroxamic acid, $CH_3—CONHOH$, to triphenylacethydroxamic acid, $(C_6H_5)_3C—CONHOH$ (p. 674). Furthermore, it is of interest to point out that the two isomeric radicals, $(C_6H_5)_2CH—C_6H_4—$ and $(C_6H_5)_3C—$, differ widely in this respect (p. 676). The former is merely a substituted phenyl, $R—C_6H_4—$, and as such it should possess a high electron attraction. This is distinctly not the case with triphenylmethyl.

The thermal decomposition of diacyl-hydrazides, $Ar—CO—NH—NH—CO—Ar'$, into ArCN, $ArNH_2$ and CO_2 (p. 594), affords a direct method for evaluating the relative electron attraction of radicals, which has been but little exploited as yet.

In the reaction:

$$R_3C—OH \longrightarrow R_2CO + RH,$$

obviously the group with the least electron attraction should be detached to form the hydrocarbon. Grignard has obtained results (p. 176) which

[44] Jones and Hurd, *J. Am. Chem. Soc.* **43**, 2428 (1921).

indicate the following series: phenyl > methyl > other alkyls > β-ethylenic, such as allyl.

Concerning the pyrolysis of phosphonium hydroxides and chlorides:

$$R_4POH \longrightarrow R_3PO + RH,$$

and

$$R_4PCl \longrightarrow R_3P + HCl + \text{olefine},$$

see p. 715. The results differ rather widely from those given in this chapter.

Physical Chemistry Considerations

Since reactions of pyrolysis usually concern but one compound, it may be assumed that many of them are unimolecular. Certainly, many of them are, but it is equally certain that many of them are not. Hinshelwood [45] has provided an interesting survey of this important field of theoretical chemistry. Studies on reaction kinetics will be mentioned throughout the monograph in their proper place, but for the most part the details must be referred to in the original articles. For example, methane, cyclopropane, acetone, phosgene, azomethane, ethoxyoxaloacetic ester and many others have been studied in this connection.

Considerations from thermodynamics are of importance in enabling one to predict the possibility or impossibility of a reaction under a given set of conditions. It is a general thermodynamic rule that the free energy change must be favorable. At least, below 1000° C. methane is the end member in the stability series of aliphatic hydrocarbons (the lowest free energy of formation per carbon atom), and the rule accounts in a qualitative way for the almost universal occurrence of methane as one of the products of thermal decomposition of aliphatic hydrocarbons. Carbon and hydrogen, as end products, are similarly explained. Likewise, the fact that acetylene is the most stable hydrocarbon at the temperature of the electric arc logically issues from the fact that it is the only hydrocarbon whose thermodynamic stability increases with increasing temperature. A satisfactory explanation for the observation that ethane fails to dissociate (R. N. Pease, private communication) at temperatures below 550-600° is that equilibrium is unfavorable, and that the reverse reaction predominates. In general, the reactions which take place depend as much on the nature of the products as on the nature of the reactants. In two recent papers, Francis has derived equations for the free energies of formation [46] of several hydrocarbons and alcohols

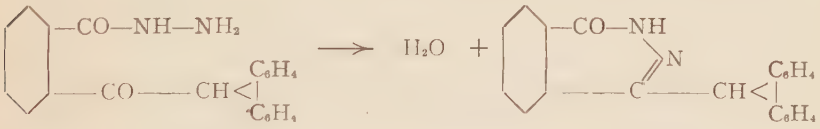
[45] Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926.
[46] Francis, *Ind. Eng. Chem.* **20**, 277, 283 (1928).

as functions of temperature. From this study, he has arrived at interesting conclusions which are consistent with the known reactions of pyrolysis. These papers are deserving of careful study.

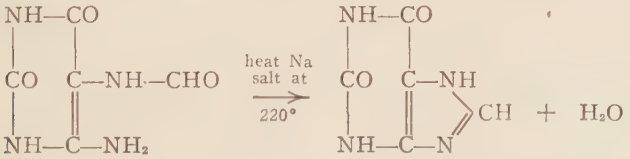
The use of the Nernst heat theorem regarding the pyrolysis of formamide has been used by Meyer [47] and by Taylor [48] (p. 583). Mathematical data on the thermal decomposition of petroleum substances are given in *Ind. Eng. Chem.* **6**, 383, 684, 472 (1914); **7**, 484, 945, 1020 (1915), and in *J. Soc. Chem. Ind.* **33**, 626 (1914).

Reactions Which Proceed Because of Two Reacting Groups in the Molecule.

Functional groups in compounds such as the carbonyl, carboxyl, amino, etc., have certain well defined reactions with other compounds or groups. Frequently it is possible to prepare a compound containing two groups in its molecule, which although potentially able to react with each other, yet fail to do so under ordinary conditions. This interaction may often be induced by heat. This is particularly true in many cases wherein water is eliminated. Some examples follow. The first, which is brought about [49] by 30 minutes' heating at 220°, resembles hydrazone formation:

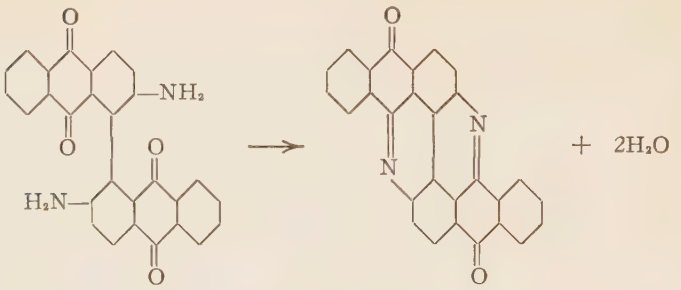


The condensation between amine and aldehyde groups is illustrated [50] in the preparation of xanthine in 60-70 percent yields:

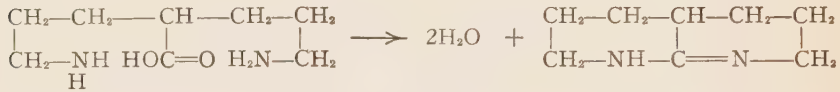


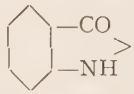
3-Methyl-xanthine may be similarly prepared. Another such reaction which apparently gives good yields [51] is the production of flavanthrene from 2,2′-diamino-1,1′-dianthraquinonyl.

[47] Meyer and Orthner, *Ber.* **54**, 1705 (1921).
[48] Taylor, *Ind. Eng. Chem.* **18**, 959 (1926).
[49] Wislicenus and Neber, *Ann.* **418**, 274 (1919).
[50] Traube, *Ber.* **33**, 3040 (1900).
[51] Scholl and Dischendorfer, *Ber.* **51**, 452 (1918).

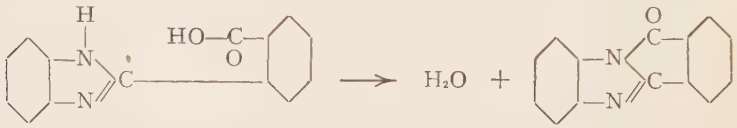


Several reactions illustrate amide or hydrazide formation, with the production of a heterocyclic ring. Distillation of bis-γ-aminopropylacetic acid [52] yields the octahydride of 1,8-naphthyridin:

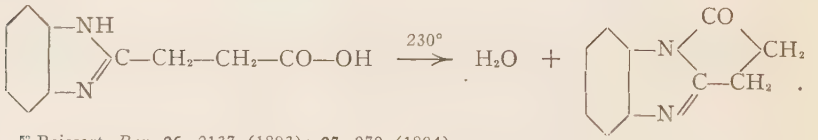


Either *o*-hydrazino-benzoic acid [53] or *o*-hydroxy-benzohydrazide [54] will produce indazolone,  , by heating, the former in excellent yields at 220-230°. Similarly, at 100°, pelletierinic acid changes [55] into its lactim, the bicyclic-2-piperolidone:

2-Phenyl-benzimidazol-*o*-carboxylic acid pyrolyzes [56] at 280-290° into *o*-benzoylen-benzimidazol;



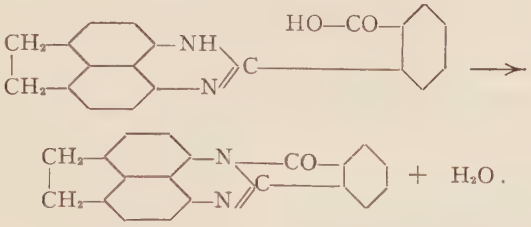
and a very similar observation was noted recently [57] by Meyer and Luders:



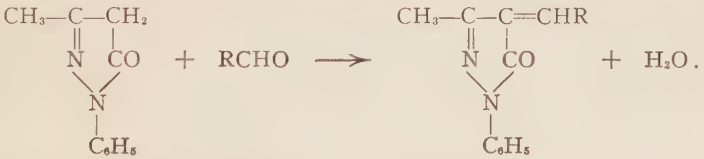
[52] Reissert, *Ber.* **26**, 2137 (1893); **27**, 979 (1894).
[53] Fischer, *Ber.* **13**, 681 (1880); *Ann.* **212**, 333 (1882).
[54] Franzen and Eichler, *J. prakt. Chem.* [2] **78**, 162 (1908).
[55] Loeffler and Kaim, *Ber.* **42**, 99 (1909).
[56] Thiele and Falk, *Ann.* **347**, 129 (1906).
[57] Meyer and Luders, *Ann.* **415**, 29 (1918).

The same authors noted anil formation from *m*-nitrophthalanilic acid at its melting point:

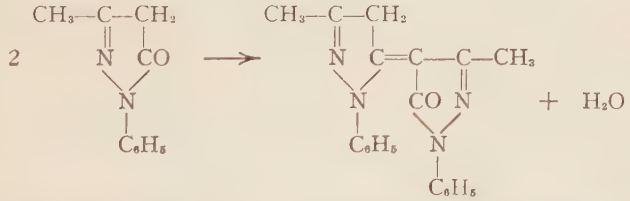
At 80° C., aceperimino-*o*-benzoic acid behaves analogously:[58]



One of the customary reactions of technical pyrazolone is condensation with aldehydes or ketones. Thus,



It will be noticed that pyrazolon contains a carbonyl group, so it occasions no surprise to learn that pyrazolon[59] reacts with itself by long heating.



Esters are used much as acylating agents; alcohols are products of the reaction. It is not customary to think of such alcohol elimination from two molecules of the ester unless some condensing agent as sodium ethylate is present. However, α-amino esters, or β-ketonic esters which are enolized to some extent, undergo self-condensation under the influence of heat. For example, the formation of diketopiperazines by heating α-amino esters[60] in a sealed tube at 160-180°.

[58] Sachs and Mosebach, *Ber.* **44**, 2852 (1911).
[59] Mohr, *Ber.* **38**, 2578 (1905); Stollé, *Ber.* **38**, 3026-30 (1905).
[60] Fischer, *Ber.* **34**, 435 (1901); **39**, 543, 557 (1906).

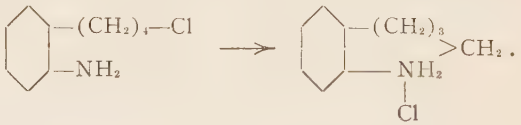
$$2R{-}CHNH_2{-}CO{-}OR' \longrightarrow 2R'OH + HN\!<\!\begin{matrix}CHR{-}CO\\ \\ CO{-}CHR\end{matrix}\!>\!NH$$

By melting dipeptides, $HO_2C{-}CHR{-}NH{-}CO{-}CHR{-}NH_2$, the same anhydride [61] is formed, and in many cases very smoothly with the elimination of water. Acetoacetic ester is decomposed somewhat into alcohol and dehydroacetic acid by long refluxing. Arndt and Nachtwey [62] have demonstrated that good yields of the latter may be secured if an apparatus is used that is capable of removing the alcohol as fast as it is formed (see p. 559).

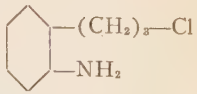
One of the most familiar reactions of the amines is their reaction with alkyl halides to produce substituted ammonium salts. This same reaction occurs readily if the amino group and the alkyl halide are both in one molecule. Ring closure is, of course, necessary in the latter case. By mere warming in aqueous solution, δ-chloro-*n*-butyl amine is transformed into pyrrolidine hydrochloride:

$$\begin{matrix}CH_2{-}CH_2Cl\\ |\\ CH_2{-}CH_2{-}NH_2\end{matrix} \longrightarrow \begin{matrix}CH_2{-}CH_2\\ |\quad\quad >NH_2Cl.\\ CH_2{-}CH_2\end{matrix}$$

A seven membered ring, hexamethylene - imine - hydrochloride,[63] $(CH_2)_6\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>\!NH_2Cl$, is likewise formed from ζ-chloro-hexylamine, although the yields are poorer. Almost quantitative yields, however, are reported [64] in a strictly analogous process, namely, the formation of homotetrahydroquinoline hydrochloride:

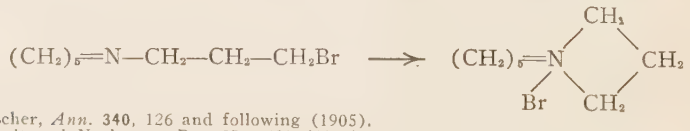


The reaction of ring closure [65] with the lower homolog,



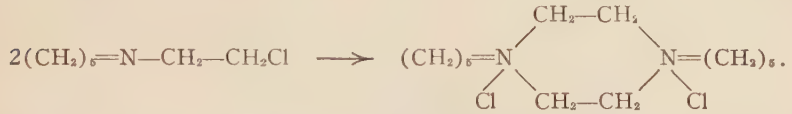
is one which takes place very readily.

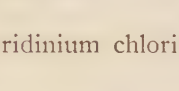
α-Piperidino-γ-bromopropane illustrates [66] the same idea. The ring-closure occurs even on standing, and trimethylene piperidinium bromide is formed.

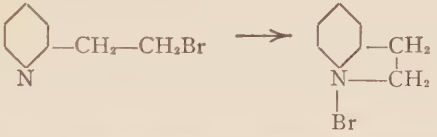


[61] Fischer, *Ann.* **340**, 126 and following (1905).
[62] Arndt and Nachtwey, *Ber.* **57**, 1489 (1924).
[63] von Braun and Steindorff, *Ber.* **38**, 3091 (1905).
[64] von Braun and Bartzsch, *Ber.* **45**, 3383 (1912).
[65] von Braun and Steindorff, *Ber.* **38**, 853 (1905).
[66] Gabriel and Stelzner, *Ber.* **29**, 2389 (1896).

The similar β-chloroethane derivative [67] reacts in hot alcohol, yielding diethylene-bis-piperidinium chloride:



Earlier, Marckwald and Frobenius [68] had assumed the formation of 1,1-ethylene piperidinium chloride,  , in this reaction, but Dunlop [69] demonstrated the correctness of the double formula. The following reaction [70] is spontaneous:



The compound,[71] γ-bromopropyl diethyl amine, $BrCH_2—CH_2—CH_2NEt_2$, soon changes on standing into a quaternary ammonium salt, presumably an 8-membered ring compound similar to Knorr and Roth's,[72] from the corresponding chloro derivative. Marvel has found also that δ-bromobutyl diethylamine changes gradually into diethyl pyrrolidinium bromide.

[67] Knorr, Hörlein and Roth, *Ber.* **38**, 3136 (1905).
[68] Marckwald and Frobenius *Ber.* **34**, 3557 (1902).
[69] Dunlop, *J. Chem. Soc.* **101**, 2000 (1912).
[70] Löffler, *Ber.* **37**, 165 (1904).
[71] Marvel, Zartman and Bluthardt, *J. Am. Chem. Soc.* **49**, 2302 (1927).
[72] Knorr and Roth, *Ber.* **39**, 1424 (1906).

Chapter 3.

Aliphatic Hydrocarbons.

Historical Development of the Pyrolysis of the Simple Hydrocarbons.

More than a century ago, Dalton and William Henry [1] subjected methane and ethylene to the continued action of electric sparks. Thirty years later, Marchand [2] established the fact that the ultimate pyrolytic resolution of a hydrocarbon into its elements could not in general be regarded as the immediate result of a simple chemical change. In Marchand's experiments large quantities of methane were observed during the decomposition of ethylene at bright red heat, and he regarded the initial stage of the pyrolysis as a simple decomposition [3] into carbon and methane:

$$C_2H_4 \longrightarrow C + CH_4.$$

This view derived some support from the observation [4] that there was little volume change when ethylene was decomposed by a platinum wire which was heated electrically to dull redness. Carbon and methane were noted as reaction products. In criticism of this otherwise important bit of evidence, V. B. Lewes has pointed out that denser hydrocarbons, both solid and liquid, are undoubtedly formed from ethylene at incipient red heat.

During the years 1863-1869, Berthelot [5] made the first systematic study of the behavior of hydrocarbons at high temperatures. As was expounded earlier (p. 17), he contended that a hydrocarbon never pyrolyzes directly into its elements, but that the primary change always involves either a polymerization such as that of acetylene to benzene, or a coalition of two or more molecules with the elimination of hydrogen to form molecules of a denser hydrocarbon, which in turn undergo a series of similar changes until carbon finally appears as the result of

[1] Dalton's "New System," vol. I, pp. 440, 447; *Phil. Trans. Roy. Soc.* **99**, 446 (1809).
[2] Marchand, *J. prakt. Chem.*, **26**, 478 (1842).
[3] *See also* Magnus, *Pogg. Ann.* **90**, 1 (1853); Quet, *Compt. rend.* **46**, 903 (1858).
[4] Buff and Hofmann, *Ann.* **113**, 129 (1860); DeWilde, *Bull. soc. chim.* [2] **6**, 267 (1866).
[5] Berthelot, *Ann. chim. phys.* [3] **67**, 53 (1863); [4] **9**, 413, 455, 471 (1866); **12**, 5, 122 (1867); **16**, 143-162 (1869); *Compt. rend.* **62**, 905; **63**, 788 (1866). *Bull. soc. chim.* **7**, 217 (1867).

the decomposition of an extremely complex molecular aggregate. Berthelot considered acetylene the ultimate compound in pyrolytic changes, and at the same time he regarded it as the chief factor in the origin of other pyrogenic hydrocarbons. To correct this faulty idea, which was generally accepted for many years, Bone and Coward [6] demonstrated that the importance of acetylene as a factor in the breaking down of hydrocarbons was much overestimated. To quote: "The detection of quite insignificant quantities of acetylene among the decomposition products in a particular experiment has far too often been put forward as satisfactory proof of its primary and predominant formation, while the presence of 20 times as much methane has been either ignored or passed over as relatively unimportant".

Berthelot also convinced himself of the reversibility of the series of changes which he postulated, a conception which was also shown to be in error. He believed that at any given high temperature there would finally be established from any particular hydrocarbon a complex state of equilibrium between hydrogen, methane, ethane, ethylene, acetylene, benzene, styrene, diphenyl, naphthalene, anthracene and carbon, but no investigator has ever demonstrated the attainment of such a state of equilibrium by quantitative measurements. Although Berthelot's conception of the mechanism of pyrolysis was faulty, his was the first serious attempt to make a comprehensive study of the behavior of compounds at high temperatures, and in so doing, he rendered a great service.

Evidence of the insufficiency of Berthelot's theory appeared only a few years after its proposal. Thorpe and Young [7] distilled solid paraffins under pressure—a process which resembles present-day "cracking"—and observed that the primary change was a scission into an olefine and a lower paraffin, without the loss of hydrogen. Moreover, in 1886, Armstrong and Miller [8] suggested the possibility of direct formation of aromatics from paraffins (e.g., benzene from hexane) without the interaction of acetylene, since acetylene hydrocarbons were almost entirely absent in compressed oil gas, but olefines and benzenes were present. Because of the isolation of various aromatic hydrocarbons (benzene to anthracene) from Russian oil residues, Anschütz [9] proposed that many of the more complex hydrocarbons were formed from the simpler aromatic hydrocarbons by hydrogen elimination. Thus:

$$2C_7H_8 \longrightarrow C_{14}H_{10} + 3H_2.$$

[6] Bone and Coward, *J. Chem. Soc.* **93**, 1198 (1908).
[7] Thorpe and Young, *Proc. Roy. Soc.* **19**, 370 (1871); **21**, 184 (1873).
[8] Armstrong and Miller, *J. Chem. Soc.* **69**, 74 (1886).
[9] Anschütz, *Ber.* **11**, 1213 (1878).

From Prunier's [10] investigations of thermal decompositions, he concluded that the degree of unsaturation of the resulting products varied not only with the temperature but also with the duration of the reaction.

Lewes [11] furnished an important contribution to the chemistry of ethylene. In his experiments ethylene was passed either alone or in the presence of hydrogen through a platinum tube, 2 mm. × 140 mm. He observed that fairly large amounts of acetylene and methane were formed, and considered that the primary stage of the decomposition yielded equal volumes of these hydrocarbons:

$$3C_2H_4 \longrightarrow 2CH_4 + 2C_2H_2.$$

This attempt to express the mechanism of pyrolysis by an ordinary chemical equation was later shown to be inadequate by Bone and Coward. Lewes found that if the products of the reaction were kept for a time in the hot zone (800-900°) aromatic hydrocarbons were formed, and that at still higher temperatures, acetylene, carbon and hydrogen resulted. Berthelot's influence on the chemistry of thermal decomposition is evident from the fact that Lewes still accepted the idea that methane is initially transformed into acetylene and hydrogen.

Haber's work in 1896 has already been mentioned. He showed [12] that at 600-700°, *n*-hexane undergoes pyrolysis into methane and amylene, without the formation of any acetylene. Also, Haber was a vigorous assailant of Berthelot's theory. Furthermore, in the rejection of the acetylene theory of the luminosity of flames, he severely criticized Lewes' work. Ipatiew [13] also demonstrated that olefines but not aromatics were formed from hexane by heating. In addition, he showed that olefines, such as ethylene and *iso*butylene, undergo polymerization reactions when heated at 70 atmospheres and at a temperature of 380-400°. Most of Ipatiew's experiments were performed in the presence of catalysts.

The investigation of Bone and Coward [14] on the pyrolysis of methane and the C_2 hydrocarbons gave results of the greatest importance. The measurements were quantitative, and especial attention was paid to the time factor. These experiments and subsequent ones will be presented in considerable detail. A concise summary dealing with "The Pyrogenesis of Hydrocarbons" is deserving of careful study; Part I, "Historical and Bibliographical" by E. Lawson Lomax, and Part II, "General Considerations" by A. E. Dunstan and F. B. Thole. This

[10] Prunier, *Ann. chim. phys.* **17**, 1 (1879).
[11] Lewes, *Proc. Roy. Soc.* **55**, 99 (1894); **57**, 394 (1895); *J. Soc. Chem. Ind.* **11**, 584 (1892). *Chem. News* **69**, 87 (1894); **71**, 273, 286, 298 (1895).
[12] Haber, *Ber.* **29**, 2691 (1896).
[13] Ipatiew, *Ber.* **37**, 2961 (1904).
[14] Bone and Coward, *J. Chem. Soc.* **93**, 1197 (1908).

and 5% nitrogen) is passed through an empty, unglazed porcelain tube of 16 mm. diameter at a rate of 4 liters per hour, there is a 3 percent expansion at 900°. At a rate of 70 liters per hour for four hours at 1050°, these authors report a yield of 6.5 grams of oil, 1.6 grams of tar and very little carbon. Similarly, but at 1100°, there is formed 9 grams of oil, 4.5 grams of tar and 1 gram of carbon. In 100 minutes at 1150°, the yield of oil is 4.2 grams; of tar, 3.5 grams; and of carbon, 3.1 grams. The gases in these experiments was stated to be chiefly methane and hydrogen, contaminated always with some acetylene and other hydrocarbons. Apparently Fischer and Tropsch did not encounter the effect of carbon monoxide formation with the porcelain tube as was noted by Bone and Coward. Many of the experiments reported by Fischer and Tropsch were performed in a packed porcelain tube. The light oil from a run wherein porcelain ring packing was used was characterized by distillation analysis (30 cc. of the oil). The distillate to 55° tures. Methane alone is formed at the lower temperature limit for the reaction, which according to Bone and Jerden [17] is about 1200°. Thus:

$$C + 2H_2 \rightleftharpoons 2CH_4.$$

Berthelot's denial [18] of the fact that methane may be directly synthesized at as low a temperature as 1200°, caused Bone and Coward [19] to repeat and to confirm the results. Furthermore, they showed that if a small quantity of pure carbon is heated for 36 hours at 1150° in a stream of pure hydrogen, a 73 percent yield of methane is formed. In this experiment a quartz-lined porcelain tube was used. Pring [20] also asserted that pure hydrogen unites with pure carbon at all temperatures above 1100°, although the velocity of the reaction is very slow even at 1500°. An equilibrium value is attained, which shows but 0.36 percent methane at 1200°. At 1000°, the gases of the equilibrium mixture,[21] approached from either side, contain 98.9 percent hydrogen and 1.1 percent methane; and at 850°, 97.5 percent hydrogen and 2.5 percent methane.

At the temperature of the electric arc [22] (3500°) carbon and hydrogen unite to form acetylene and ethane as well as methane. The yield of acetylene is poor because it depends on the rate of cooling, and no method has been developed to cool the hot gases with sufficient rapidity. Butane and liquid hydrocarbons are not formed. (See p. 52.)

[15] Lebeau and Picon, *Compt. rend.* **179**, 1059 (1924); *Chem. Abstracts* **19**, 915 (1925).
[16] Journiaux, *Bull. soc. chim.* **33**, 260 (1923).
[17] Bone and Jerden, *J. Chem. Soc.* **71**, 41 (1897); **79**, 1042 (1901).
[18] Berthelot, *Compt. rend.* **40**, 905 (1905); *Ann. chim. phys.* [8] **6**, 183 (1905).
[19] Bone and Coward, *J. Chem. Soc.* **93**, 1975 (1908).
[20] Pring, *J. Chem. Soc.* **97**, 498 (1910); Pring and Fairlie, *ibid.* **101**, 91 (1911).
[21] Coward and Wilson, *J. Chem. Soc.* **115**, 1380 (1919).
[22] Bone and Jerden, *loc. cit.*; Contardi, *Atti congresso naz. chim. ind.* **1924**, 358-370; *Chem. Abstracts* **19**, 1941 (1925).

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$$3C_2H_4 \longrightarrow 2CH_4 + 2C_2H_2.$$

This attempt to express the mechanism of pyrolysis by an ordinary chemical equation was later shown to be inadequate by Bone and Coward. Lewes found that if the products of the reaction were kept for a time in the hot zone (800-900°) aromatic hydrocarbons were [illegible] acetylene, hydrogen and and this may account for the dense nature of the carbon which it produces. The decomposition of the other three hydrocarbons is not a surface effect, but instead it occurs throughout the main body of the gas. Bone and Coward suggest that the metallic luster of coke is due to the surface decomposition of methane at the high temperature at which it is maintained.

At 1000°, porcelain is reduced by methane, and in consequence porcelain tubes should not be used where quantitative results are desired. Whereas quicklime gives only 2.8 percent of carbon monoxide in one hour at 1000°, porous porcelain yields as high as 22 percent. The following data, relative to the decomposition of methane, are of interest.

TABLE I. *Decomposition of Methane.*

Temperature °C.	Duration Minutes	Hydrogen Formed Percent	Methane Remaining Percent	Other Pertinent Facts
985	1	8.8	90.4	.....
1015	60	51.2	48.2	.....
1015	25	...	1.9	Tube packed with quicklime
1150–60	1	54.9	44.6	0.5 percent of C_2H_2 observed
1150–60	5	72.25	27.25	No acetylene
1150–60	60	77.7	22.3	.....
1150–60	180	90.85	9.15	.....

Fischer and Tropsch [25a] have recently reported experiments on methane at 900-1150° that are noteworthy. If the gas (93% methane

[23] Bone and Wheeler, *J. Chem. Soc.* **81**, 542 (1902).
[24] Bradley and Parr, *Chem. & Met. Eng.*, **27**, 737 (1922).
[25] Bone and Coward, *J. Chem. Soc.* **93**, 1206 (1908).
[25a] Fischer and Tropsch, *Brennstoff Chemie* **9**, 309-316 (1928).

and 5% nitrogen) is passed through an empty, unglazed porcelain tube of 16 mm. diameter at a rate of 4 liters per hour, there is a 3 percent expansion at 900°. At a rate of 70 liters per hour for four hours at 1050°, these authors report a yield of 6.5 grams of oil, 1.6 grams of tar and very little carbon. Similarly, but at 1100°, there is formed 9 grams of oil, 4.5 grams of tar and 1 gram of carbon. In 100 minutes at 1150°, the yield of oil is 4.2 grams; of tar, 3.5 grams; and of carbon, 3.1 grams. The gases in these experiments was stated to be chiefly methane and hydrogen, contaminated always with some acetylene and other hydrocarbons. Apparently Fischer and Tropsch did not encounter the effect of carbon monoxide formation with the porcelain tube as was noted by Bone and Coward. Many of the experiments reported by Fischer and Tropsch were performed in a packed porcelain tube. The light oil from a run wherein porcelain ring packing was used was characterized by distillation analysis (30 cc. of the oil). The distillate to 55° adds bromine and mercuric acetate and represents 7.8 percent of the total; between 55-85°, the benzene fraction, 61.1 percent; to 115°, 12.6 percent; to 145°, 3.9 percent; above 145°, 14.6 percent. Benzene, toluene, xylene and naphthalene are all present.

The thermal decomposition of methane by an incandescent wire (platinum bands, 0.01 mm. thick, coated with a mixture of CaO : BaF_2 (1 : 10)) is strictly monomolecular. Thus, dp/dt is proportional to p. Only the methane molecules which collide with the wire are decomposed.[26] It may be calculated from the heat of activation that:

$$CH_4 + 19\ \text{Cal.} \longrightarrow C + 2H_2.$$

In view of the fact that methane is so stable to heat alone, it is interesting to note that thermodynamical calculations[27] indicate that its decomposition into carbon and hydrogen should be almost complete at 700°. From an initial system of methane, ethane or ethylene, at temperatures above 400°, Cantelo concludes that the final equilibrium will be a system of methane, hydrogen and carbon. The results of Bone and Coward support this conclusion, and also the results of Sabatier and Senderens,[28] who performed the decompositions in the presence of nickel. In the latter case, the decomposition of methane begins at 390°.

A novel way to produce[29] a mixture of carbon monoxide and hydrogen is to pyrolyze methane in a heated retort and to expose the carbon which is thereby produced to the action of superheated steam. To obtain hydrogen and hydrocarbons, mainly olefinic, from methane,

[26] Schwab and Pietsch, *Z. physik. Chem.* **121**, 189 (1926); *ibid.* **126**, 473 (1927).
[27] Cantelo, *J. Phys. Chem.* **28**, 1026 (1924); **30**, 899, 1641 (1926); **31**, 124, 246, 416 (1927).
[28] Sabatier and Senderens, *Compt. rend.* **124**, 616 (1898); **131**, 267 (1900).
[29] Spear, Can. 264,324, Sept. 14, 1926. *Chem. Abstracts* **20**, 3697.

it is suggested in a recent patent [30] that a thin (1 mm.) stream of methane be gradually and uniformly heated to 950°, and the reaction products kept under reduced pressure (20 mm.) till they are completely cooled.

From a study of the behavior of a great variety of hydrocarbons, both aliphatic and aromatic, to an explosive electric discharge (which produces not only very great thermal effects but also possibly some electrical effects), Contardi [22] found that the gaseous mixture in all cases was of the same composition. This indicates a similarity in the ultimate reactions in all cases. The analytical data show that one of these ultimate reactions, namely, the decomposition of methane or ethane into acetylene and hydrogen, proceeds with enormous velocity in the hot zone of the arc:

$$2CH_4 \longrightarrow C_2H_2 + 3H_2, \quad \text{and} \quad C_2H_6 \longrightarrow C_2H_2 + 2H_2.$$

Simultaneously, methane and ethane are constantly being synthesized in the cold zone (1200°) at the expense of the carbon already formed:

$$C + 2H_2 \longrightarrow CH_4, \quad \text{and} \quad 2C + 3H_2 \longrightarrow C_2H_6.$$

Methane and ethane appear in the final gas since they do not pass through the hot zone after their synthesis. From hexane, an initial yield of 18 percent of acetylene in the gas augments to 33-34 percent on continued discharge.

Pyrolysis of Ethane.

Viewed as a "methano-alcohol" (p. 22), ethane should pyrolyze in two ways, depending on whether methane or hydrogen is to be eliminated from the molecule. Methane, ethylene and hydrogen should be the primary products of the reaction on this basis. From the viewpoint of electron attraction of radicals (p. 26), ethane should dissociate not only at the carbon-to-carbon linkage but also at the C—H linkages. Thus:

$$CH_3—CH_3 \longrightarrow 2[CH_3—] \longrightarrow CH_4 + [CH_2=],$$

or

$$C_2H_6 \rightleftharpoons [C_2H_4] + 2[H] \rightleftharpoons [C_2H_2] + 4[H] \longrightarrow 2C + 6[H].$$

The methylene or ethylene radicals should appear temporarily as ethylene, and the hydrogen radical would be expected either to appear as molecular hydrogen or to reduce the other radicals.

Bone and Coward's [14] theory to explain the facts of the pyrolysis of ethane is much like the foregoing. It is also applicable to the pyroly-

[30] Brit. Pat. 261,267, Apr. 29, 1926; *Chem. Abstracts* **21**, 3368 (1927).

sis of ethylene and acetylene. The residues, [CH_2=], [HC≡] and possibly [CH_3—] which are considered to be formed by direct rupture of the carbon-to-carbon bonds in ethylene, acetylene and ethane respectively, are of fundamental importance, but in the case of ethane and ethylene it is considered that the primary effect of high temperature is one of dehydrogenation. The residues, or radicals, are formed concurrently. There are three ways for the residues to terminate their fugitive existence. They may become dehydrogenated further into carbon and hydrogen; they may unite with themselves; or, because of a hydrogen-rich atmosphere, they may accept hydrogen to form methane. Bone and Coward point out that this theory, which postulates radicals capable of hydrogenation, is the only one which can explain the existence of such large amounts of methane from ethane, ethylene and acetylene as are actually observed in practice.

With a sample of ethane,[31] analyzing 83.2 percent ethane, 15.2 percent methane and 1.6 percent nitrogen, a 5 percent increase in volume appears after 12 seconds contact time in a small pyrex bulb at 650°. The volume percentage composition of the final gaseous mixture follows: unsaturated hydrocarbons 6.5 percent; hydrogen 6.5 percent; methane 15.2 percent; and the remainder ethane and nitrogen. In other words, since approximately this quantity of methane was present at the start, the conversion into methane with these conditions is very slight. It is less than 1 percent of the original volume. The actual volumes of the gaseous products from 250 cc. of ethane or from the same volume in dilution with 125 cc. of nitrogen are very similar, showing the inertness of nitrogen as a diluent. The volume percentage conversion values in this case are 8.0 percent unsaturated; 8.8 percent hydrogen; and no methane. Pease [32] finds that the equilibrium:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2,$$

corresponds to 17.5 percent dissociation at a temperature of 600° and 1 atmosphere pressure; 27.5 percent at a temperature of 650° and 1 atmosphere pressure; and 41 percent at a temperature of 700° and 1 atmosphere pressure. At 700°, many interfering details present themselves, making equilibrium studies difficult.

Frey and Smith [33] have conducted experiments with ethane in a 400 cc. round, clear silica flask, covered with a heavy copper sheath, and heated in an electric furnace. Like Pease, they find that at 575°,

[31] Pease, Princeton University, private communication, 1927.
[32] Pease, *J. Am. Chem. Soc.* **50**, 1782 (1928); *also* private communication, 1928. Pease and Durgan, *J. Am. Chem. Soc.* **50**, 2715 (1928).
[33] Frey and Smith, private communication 1928; published with the permission of the Director of the Bureau of Mines.

during the first part of the pyrolysis, the only appreciable reaction is that of simple dehydrogenation into ethylene. Starting with ethane of 99.8 percent purity (0.2 percent nitrogen), the analysis of products after 4 minutes' heating (575° and 760 mm.) is: ethane 91.5 percent; ethylene 4.1 percent; hydrogen 4.2 percent; no methane. Furthermore, the reaction is approximately unimolecular since the same fraction of ethane is converted into ethylene at 393 mm. as at 760 mm.

The following data on the thermal decomposition of ethane are taken from the paper of Bone and Coward. Nearly 35 percent of ethane is still recoverable after 30 minutes at 675°, and 2 percent still persists after 6 hours. At 810°, however, all but 18 percent pyrolyzes during the first minute, and in 15 minutes its presence is not detectable.

TABLE II. *Pyrolysis of Ethane at 810°.*

Time in minutes.....	1	5	15	30	60
			Percent		
Ethane	17.90	2.40	....	....	....
Ethylene	11.20	4.40	0.75	....	....
Methane	31.30	54.55	64.65	66.0	63.75
Hydrogen	37.70	37.45	34.10	34.0	36.25
Acetylene	1.90	1.20	0.50	....	....

At 1140-1185°, ethane scarcely survives one rapid passage through the hot tube. After 5 minutes' heating, much carbon appears, and analysis of the gases shows 27 percent CH_4 and 73 percent H_2; in 60 minutes, analysis reveals 6 percent CH_4 and 94 percent H_2. Obviously, the large amount of hydrogen formed at this high temperature comes as the result of the pyrolysis of methane, after its formation from ethane.

When ethane is diluted with three volumes of nitrogen, and the mixture circulated for an hour at 800°, 18.15 percent of methane (mean value) is in the gaseous mixture. The result very nearly conforms to the equation:

$$C_2H_6 + 3N_2 \longrightarrow CH_4 + H_2 + C + 3N_2.$$

It is well to recall that methane decomposes very slowly at this temperature. If ethane is pyrolyzed in the presence of three volumes of hydrogen instead of nitrogen, 80 percent of the carbon in the original ethane appears as methane:

$$C_2H_6 + 3H_2 \longrightarrow 2CH_4 + 2H_2.$$

Both of these experiments furnish good evidence for the probable temporary existence of radicals and of their hydrogenation to methane.

Hollings and Cobb [34] have also reported that ethane decomposes rapidly at 800°, but that some still remains after 46 seconds. The chief

[34] Hollings and Cobb, *J. Gas Lighting* **126**, 917 (1914); *Chem. Abstracts*, **8**, 3110 (1914).

organic products of the reaction are methane and ethylene. Bradley and Parr [24] have noted that the C_2 hydrocarbons, ethane, ethylene and acetylene, not only serve as mechanical diluents in the pyrolysis of such hydrocarbons as xylene, but also exert a large chemical effect at temperatures above 600°. They consider that these hydrocarbons are entirely decomposed above 725°, but unless catalysts are present this figure seems somewhat low. A recent patent [35] describes the production of ethylene by heating ethane (from natural gas) above 500°.

Recent work on the pyrogenic decomposition of ethane is that of Williams-Gardner,[36] who employed a circulation apparatus, similar to that of Bone and Coward. He prefers to think that dissociation into radicals precedes dehydrogenation, but otherwise accepts the mechanism proposed by Bone and Coward. According to Williams-Gardner, ethane is stable at 500°. It begins to dissociate reversibly at 550°, and the methyl radical thus produced is transformed into the methylene radical at temperatures above 600°. Ethylene is an important product of the reaction to 700°, but at higher temperatures this again becomes dissociated into methylene or dehydrogenated into [HC≡]. At all temperatures (550-850°) these radicals are irreversibly reduced to methane, and above 850° the dominant equilibrium is that of methane with carbon and hydrogen. These results may be summarized as follows:

$$CH_3{-}CH_3 \overset{550°}{\rightleftharpoons} 2[CH_3{-}] \overset{\text{above } 600°}{\rightleftharpoons} 2[CH_2{=}] + H_2 \underset{650\text{-}850°}{\overset{550\text{-}700°}{\rightleftharpoons}} C_2H_4 + H_2$$

$$2[CH_2{=}] \rightarrow 2[CH{\equiv}] + H_2$$

Then

$$[CH_3] \text{ or } [CH_2] \text{ or } [CH] \underset{550\text{-}850°}{\overset{H_2}{\longrightarrow}} CH_4 \overset{\text{above } 850°}{\rightleftharpoons} C + 2H_2.$$

Bone and Coward observed that 0.05 gram of naphthalene, but no benzene, is formed from 1.20 grams of ethane at 675°. Only half a gram of condensable hydrocarbons appear from 13 grams (10 liters) of ethane when this gas is passed rapidly through a tube at 1000°. Somewhat different results were observed by Williams-Gardner. He found considerable aromatic formation in the neighborhood of 750°, but agreed with Bone and Coward that acetylene plays a negligible part in this change. Instead, the formation of aromatic hydrocarbons is caused by the behavior of ethylene at this temperature. This is a predominant secondary change and will be taken up somewhat more fully under ethylene.

[35] Haynes and Curme, U. S. Pat. 1,460,545, July 3, 1923; *Chem. Abstracts* **17**, 2886 (1923).
[36] Williams-Gardner, *Fuel in Science and Practice*, **4**, 430 (1925).

Pyrolysis of Ethylene.

Ethylene is stable [37] at 344°. It undergoes considerable decomposition at 570°. This reaction has been studied in considerable detail by Bone and Coward and has been found to be very complex. The results are quite intelligible, however, if the mechanism suggested by these investigators is accepted, namely, that there is dehydrogenation to acetylene and simultaneous scission into the radicals $[CH_2=]$ and $[HC\equiv]$. It has already been shown how these radicals, in the presence of hydrogen, may react further to produce the substances which are actually formed.

The methane system of compounds would also predict, as a primary reaction, the formation of acetylene and hydrogen, since ethylene is the "formaldehyde of the methane system". Thus:

$$CH_2=CH_2 \longrightarrow C_2H_2 + H_2,$$

just as

$$CH_2=O \longrightarrow CO + H_2.$$

It is obvious that this simple equation for the pyrolysis of ethylene cannot be expected to hold rigorously.

The reactions of ethylene which are induced by heat may be conveniently classified under three headings:

(a) Methane, ethane, acetylene and hydrogen. The mechanism for this conversion has already been outlined. At temperatures which are sufficiently low to preserve the ethane and acetylene, a noticeable quantity of ethylene also invariably persists.

(b) Butadiene and aromatic hydrocarbons. Very little carbon is formed (except at the higher temperatures), which is in contrast to the behavior of ethane.

(c) Polymerization reactions at high pressures.

The data [38] in Table III summarize the results of the pyrolysis of ethylene at 570-580° in a circulation apparatus.

Table III. *Composition of the Gases from the Pyrolysis of Ethylene at 570-580°.*

Time in minutes	Start	2	15	30	45	60	75	150
	Percent							
C_2H_4	100	75.2	49.3	40.4	34.2	29.8	27.5	24.4
C_2H_2	...	11.9	7.4	5.8	6.4	7.5	9.0	6.7
H_2	...	4.9	20.3	26.3	28.9	29.1	28.5	27.2
CH_4	...	4.4	15.2	19.1	22.0	25.7	28.0	38.8
C_2H_6	...	3.5	8.0	8.3	8.4	7.8	7.0	2.9
Total pressure mm.	365	362.5	359	354	350	350	342	342
Units of carbon in the gas ...	730	672.7	519	454	421	406	393	365

[37] Day, *Am. Chem. J.*, 8, 153 (1886).
[38] Bone and Coward, *J. Chem. Soc.* 93, 1216 (1908).

The units of carbon in the gas are calculated from the number of carbon atoms in the molecule and the partial pressure of each hydrocarbon. Thus, the figure 730 is obtained as follows: $2 \times 365 \times 1 = 730$, and the figure 365 as follows:

$$\begin{aligned} C_2H_4 &= 2 \times 342 \times .244 = 166.9 \\ C_2H_2 &= 2 \times 342 \times .067 = 45.8 \\ CH_4 &= 1 \times 342 \times .388 = 132.7 \\ C_2H_6 &= 1 \times 342 \times .029 = 19.8 \\ \text{Total} &= 365.2 \end{aligned}$$

The important features of these data are:

1. Acetylene forms rapidly at the start, and since ethylene is constantly present, acetylene persists throughout. The percentage of acetylene is greater from ethylene than from ethane.

2. The percentage of hydrogen increases rapidly during the first 15 minutes, slowly thereafter to 60 minutes, and decreases somewhat afterwards.

3. The percentage of methane increases constantly, but in the first 30 minutes, the rate of accumulation of methane is about one third the rate of loss of ethylene (67.5 mm. of CH_4 gained, to 222 mm. of C_2H_4 lost). Therefore, Lewes' equation;

$$3C_2H_4 \longrightarrow 2C_2H_2 + 2CH_4,$$

cannot represent the primary stage of the decomposition since this calls for a two thirds relationship. Neither, however, is Marchand's equation:

$$C_2H_4 \longrightarrow C + CH_4,$$

representative of fact.

4. Less than 1 percent of the carbon in the original gas separates as free carbon. Since the carbon content of the gaseous portion diminishes to half of the original value in 2.5 hours, this is indicative of the relatively large amount of tars and aromatic hydrocarbons which are formed. The formation of hydrogen *without* the corresponding separation of carbon is further evidence against Lewes' equation. Due to the stability of methane at this temperature, the hydrogen would necessarily have to come from the acetylene were Lewes' equation correct, but this would necessitate the production of carbon.

Bone and Coward also conducted experiments at higher temperatures. At 700-720°, 27 percent of the ethylene remains after 30 minutes; there is formed 37 percent of methane, 21.3 percent of hydrogen and 2.4 percent of acetylene. Acetylene is, of course, less stable at this temperature, but otherwise the results are similar to those at 570°. At 800°, 90 percent of the original ethylene disappears in 15 minutes.

These conditions are such that nearly all of the methane which is formed should be retained. The results are summarized in Table IV.

TABLE IV. *Composition of the Gases from the Pyrolysis of Ethylene at 800°.*

Time in minutes.....	1	5	15	30
			Percent	
Ethylene	57.25	21.40	9.65	0.9
Acetylene	3.00	3.90	3.85	...
Hydrogen	7.10	17.00	20.75	31.4
Methane	29.40	53.40	64.45	67.7
Ethane	3.25	5.00	1.30	...

At 800°, more carbon and less aromatics separate than at 570°. The ratio of CH_4/H_2 is about 3, in contrast to the value of about 1 at 570°, which may indicate a more rapid utilization of the hydrogen at 800° in reducing the radicals. On dilution with three volumes of nitrogen, or with three volumes of hydrogen, ethylene pyrolyzes in an hour at 800° to yield 13.8 percent and 43.5 percent, respectively, of methane. Under these conditions, ethylene and acetylene should all be destroyed but nearly all of the methane should remain intact. The ratio of $43.5/13.8 = 3.15$ indicates how very active hydrogen is at 800°.

Nine-tenths of the ethylene disappears in 1 minute at 950°, and nearly all of it in 15 minutes. Much carbon is formed, but not more than 4 percent of the gas is transformed into condensable products. The chief products of the reaction are methane and hydrogen, with the ratio CH_4/H_2 never exceeding 1.65. Because of the continuous secondary decomposition of methane, this ratio rapidly diminishes with increasing time. The data in Table V, taken at a temperature of 1180°, reveal little more than a rapid conversion of ethylene into carbon, hydrogen and methane.

TABLE V. *Composition of Gases from the Pyrolysis of Ethylene at 1180°.*

Time in minutes.....	5	15	60	240
		Percent		
Ethylene	1.75	0.70	...	...
Acetylene	0.50	....	...	...
Methane	25.20	23.35	16.1	5.8
Hydrogen	72.55	75.95	83.9	94.2

Lewes [39] demonstrated that a platinum tube has no especial effect on the pyrolysis of ethylene. He reported very little decomposition below 800°. Between 800-900° methane was produced in quantity, according to Lewes, and at 1200° hydrogen was first noticed. At 1500°, the decomposition into carbon and hydrogen was practically complete. Obviously, these temperatures are all considerably higher than those

[39] Lewes, *Proc. Roy. Soc.* 57, 394 (1895); *see also*, p. 48.

reported by Bone and Coward. One important result of Lewes' work is the observation that diluents, except when present to the extent of 75 percent or more, have very little effect in retarding the amount of decomposition of ethylene. A conclusion to be drawn from this is that radiant heat is the chief cause of the decomposition, rather than contact with heated surfaces. Lewes also noted that an increase in the rate of flow (through a platinum tube, 736 × 14 mm.) diminishes the extent of decomposition, an effect which is most apparent when the heated area is small. The data are presented in Table VI.

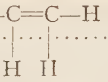
TABLE VI. *Decomposition of Ethylene with Varying Rates of Flow at 900°C.*

Length of tube heated, in inches	1	6	18
Rate of flow (cc./min.)		Percent	
5	80.1	85.48	93.76
15	70.83	79.42	90.31
40	50.58	63.17	87.15

With nickel as a catalyst,[40] ethylene decomposes at about 325° into carbon and into ethane, methane and hydrogen, these gases being formed in the ratio of 6:3:1. A longer column of nickel has practically the same effect as a higher temperature, since both induce an almost complete conversion into carbon and methane. This experiment with catalysts is interesting in comparison with the above experiments in which catalysts were absent.

Very recently, Walker [41] has reported the observation that ethylene is scarcely affected up to 600° when passed through an empty Jena tube, but fifty degrees higher than this, reaction is apparent. In this process (650°), there is a diminution in gaseous volume (970 cc. from an original 1100 cc.) when the rate of flow is 17 cc. per minute. The analysis of the effluent gas is as follows; ethylene 83.5 percent, acetylene 3.9 percent, hydrogen 3.1 percent, methane 4.2 percent, ethane 2.9 percent. With a slower rate of flow, namely, 12.2 cc. per minute, the diminution in volume is less (530 cc. from 550). The analysis of the gas follows; 67.5 percent ethylene, 8.2 percent acetylene, 4.4 percent hydrogen, 12.0 percent methane, and 6.5 percent ethane. In each case, there is some polymerization into liquid products. Apparently, no one constituent in the Jena glass (each applied separately in finely divided state) is a catalyst for the polymerization of ethylene or acetylene, but Walker believes that a combination of two or more of the oxide constituents may be the responsible factor.

[40] Sabatier and Senderens, *Compt. rend.* **124**, 616, 1358 (1897); **131**, 267 (1900). For review, *see* Malisoff and Egloff, *J. Phys. Chem.* **23**, 105, 113 (1919).
[41] Walker, *J. Phys. Chem.* **31**, 961 (1927).

Walker suggests that the decomposition of ethylene according to the scheme:  proceeds to a greater extent than scission between the double bonds, and greater also than scission between the triple bonds of acetylene.

Butadiene is an interesting product from the pyrolysis of ethylene, which was not mentioned by Bone and Coward although Berthelot obtained it in this manner in 1866, and Norton and Noyes [42] in 1886. The reaction:

$$2C_2H_4 \longrightarrow H_2 + CH_2{=}CH{-}CH{=}CH_2,$$

involves no volume change; therefore, pressure can have no effect on it. The optimum temperature for its formation is 750°. None is formed below 600°, nor can any exist above 900°. At 750°, the yield [43] is nearly 1 percent. Zanetti [43] pointed out that butadiene may be an important intermediate product in the production of aromatic hydrocarbons, since they are formed in large quantities from ethylene at 750°. In fact, over 40 years ago, Norton and Noyes ascribed the formation of aromatic hydrocarbons to olefines and diolefines, since they found no acetylene when ethylene was passed through a red hot tube. The work of Staudinger [44] lends some support to the view that butadiene is the essential intermediate in the formation of aromatics. At 800°, from 19 grams of butadiene there is formed 6 grams of tar, 30.6 percent of which is benzene, 24.5 percent naphthalene (chiefly), 16.5 percent anthracene (chiefly), and 28.5 percent other fractions.

The influence of heat and high pressure on ethylene is quite different [45] from that of heat alone. Under a pressure of 70 atmospheres, ethylene begins to polymerize at 325°, and at 380-400° the polymerization is so rapid that there is a diminution in pressure of 5 atmospheres per minute. At the conclusion of this pressure change, the pressure (after cooling) is but 25-30 atmospheres. From the gray-green liquid there may be isolated saturated hydrocarbons from pentane to nonane, naphthenes from nonanaphthene to pentadecanaphthene, small amounts of amylene and hexylene, but no benzene. Analysis of the liquid shows 52.8 percent C_nH_{2n}, 4.2 percent H_2, 43 percent C_nH_{2n+2}. Without pressure there is no such polymerization, regardless of the temperature.

[42] Norton and A. A. Noyes, *Am. Chem. J.* **8**, 362 (1886).

[43] Zanetti, Suydam and Offner, *J. Am. Chem. Soc.* **44**, 2036 (1922). *See* Birch, *Ind. Eng. Chem.* 20, 474 (1928) for the preparation of butadiene by the vapor phase cracking of oils; as the condensate from oil gas it is named "railway hydrocarbon."

[44] Staudinger, Endle and Herold, *Ber.* **46**, 2467 (1913).

[45] Ipatiew, *Ber.* **44**, 2978 (1911).

Pyrolysis of Acetylene.

Acetylene is the "carbon monoxide of the methane system" (p. 24). Since carbon monoxide is stable at high temperatures, no relationship for the mode of pyrolysis of acetylene can be drawn on this basis. However, it is interesting to note that both of these compounds may be directly synthesized from their elements at the temperature of the electric arc (see p. 49). Whereas methane is the most stable hydrocarbon at 600-800°, acetylene is the most stable hydrocarbon at the temperature of the electric arc.

The mechanism proposed by Bone and Coward for the decomposition of ethane and ethylene is equally applicable to acetylene. Furthermore, it gives a satisfactory picture of the actual facts of the case. With this plan, it is considered that acetylene dissociates into the residue [HC≡], which may react further in one of three ways. It may polymerize; it may decompose into carbon and hydrogen; or it may become hydrogenated to methane, ethylene or ethane. All three of these type reactions are met in practice.

The earliest systematic investigation of the action of heat on acetylene was by Berthelot.[46] He observed its polymerization to benzene as has been mentioned previously (p. 17). The principal change at 480-500° is one of polymerization.[47] After 20 hours of circulation through a Jena glass tube, filled with fragments of porous porcelain, 48 percent of the acetylene is polymerized, 39 percent is decomposed into carbon and hydrogen, whereas most of the remainder is reduced to ethylene, ethane and methane. Some unchanged acetylene still persists. In 8.5 hours at 650°, 60 percent polymerizes, 30 percent undergoes decomposition into carbon and hydrogen, and 10 percent appears as a hydrogenized product. There is still a small quantity of unchanged acetylene, but less than in the former case. At 700°, through a tube (70 cm. × 2 cm.) well packed with porcelain or quartz, acetylene [48] is found to yield 10-40 percent of polymeric compounds which contain benzene, small amounts of toluene and naphthalene and a considerable quantity of heavier hydrocarbons. From the latter may be isolated a little pyrene and dihydroanthracene. The packing seems to prevent the propagation of the decomposition of acetylene into carbon and hydrogen. Somewhat better yields of aromatic compounds are formed by inserting a water-cooled copper tube inside the hot tube. In this case, the optimum temperature is 950°, but the results are not considered to

[46] Berthelot, *Ann. chim. phys.* [4] **9**, 445-483 (1866).
[47] Bone and Coward, *J. Chem. Soc.* **93**, 1220 (1908).
[48] Kovache and Tricot, *Chimie & industrie* **13**, 361, 537 (1925).

indicate any possibility of commercial synthesis of benzene from acetylene.

Acetylene starts to decompose at 450°, by passing it through an empty Jena tube;[49] ethylene is more stable, since it is practically unchanged in an experiment of similar type till 615°. The following data pertain to the passage of acetylene through an empty Jena tube.

TABLE VII. *Pyrolysis of Acetylene in Empty Jena Glass Tube.*

Temperature	Rate of Flow	Original Volume of Gas	Volume of Gas Evolved	Composition of Effluent Gas		
				C_2H_2/C_2H_4	H_2	C_2H_4
°C.	cc./min.	cc.	cc.	Percent		
450	13.8	970	920	94.0/5.2		
	25	1630	1630	96.3/2.2		
500	12.5	1000	675	93.8/3.4	1.3	0.7
	33	1500	1320	93.8/5.3		
550	14.2	2200	1220	87.6/7.8		

Walker suggests that since acetylene is more inert towards decomposition at 550°, which is 100° higher than its critical temperature of pyrolysis, than ethylene is at 645°, which is 30° higher than its critical temperature of pyrolysis, that it is more simple to open up the bonds for polymerization between C≡C than to sever the bond between H—C. However, since carbon is deposited on the tube wall, he believes that acetylene breaks in part according to the scheme: .

Acetylene pyrolyzes very rapidly at 800° according to Bone and Coward. Furthermore, it invariably flashes once (but not thereafter) on entering the hot vacuous tube, unless the gas is diluted with nitrogen (or hydrogen). Because of the flashing, it seems certain that the temperature momentarily must have been much higher than that indicated by the pyrometer. However, at the end of one minute, 25 percent of acetylene is still undecomposed. Table VIII indicates this fact. Even

TABLE VIII. *Composition of Gases from the Pyrolysis of Acetylene at 795-800°.*

Duration in minutes....	1	5	15	60
	Percent			
Acetylene	25.90	7.3	1.35	...
Ethylene	4.20	2.7	....	...
Ethane	2.65	0.7	....	...
Methane	15.00	35.3	37.65	43.0
Hydrogen	52.25	54.0	61.00	57.0

at this elevated temperature, slight evidence of polymerization still persists. The important feature seems to be the large formation of

[49] Walker, *J. Phys. Chem.* **31**, 961 (1927).

methane (43 percent in one hour), which is difficult to explain except on the supposition of the direct hydrogenation of the [HC≡] radicals. This view is confirmed by the fact that nearly 5 times as much methane is present in the gas after acetylene is heated for an hour at 800° in dilution with three volumes of hydrogen as with three volumes of nitrogen; 27.35 percent and 5.65 percent of methane are formed respectively.

At 1000°, all but 1.85 percent of the acetylene is destroyed in 5 minutes, and if the reaction is allowed to progress for one hour, the record merely becomes one of the pyrolysis of methane at that temperature. Similarly, at 1150°, only 0.3 percent survives after 5 minutes' heating. Comparative experiments indicate that at 800°, 1000° and 1150°, about 19, 7.5, and 5 percent respectively of the acetylene undergoes polymerization. In these experiments on polymerization in which a continuous gas stream (4 liters per hour) is used, the gaseous products give the analytical values shown in Table IX.

TABLE IX. *Composition of Gases from the Pyrolysis of Acetylene at 1000°.*

Temperature	800°	1000°	1150°
	Percent		
Acetylene	1.35	1.55	....
Ethylene	0.45	2.60	....
Ethane	0.50	....	....
Methane	34.20	36.00	23.45
Hydrogen	63.50	59.85	76.55

The most favorable polymerization temperature, as stated above, is 600-700°, or 950° if internal cooling is employed. According to Pring [50] acetylene quickly pyrolyzes at 1500° into methane and ethylene, and, although the methane decomposes into carbon and hydrogen, it does not do so rapidly. Between 1200-1400° traces of the ethylene which is formed also persist.

It is interesting to record [51] that if acetylene is passed at 650° over activated wood charcoal, about 70-80 percent of the gas is converted into a tar, nearly half (45 percent) of which boils below 150°; 13.9 percent boils at 150-250°; and 29 percent boils between 104-300° at 13 mm. pressure. Pure benzene may be isolated from the first fraction in amounts equivalent to 13 percent of the tar.

As is well known, acetylene possesses not only the property of reaction with itself, but also of uniting with other compounds at high temperatures. Passing references only will be made to the pyrogenic formation of pyrrole and ammonium cyanide from acetylene and

[50] Pring, *J. Chem. Soc.* **97**, 498 (1910).
[51] Zelinski, *Compt. rend.* **177**, 882 (1923).

ammonia [52]; of thiophene, from acetylene and boiling sulfur [53]; of pyrazole [54] from acetylene and diazomethane; of propylene,[55] from acetylene and methane at 200° in the presence of catalysts; and of other pyrogenic condensations [56] of acetylene. The amorphous product, $3C_2H_2.4KHSO_4$, obtained by passing acetylene into fuming sulfuric acid followed by neutralization with potassium hydroxide, gives fair yields of phenol [57] when it is heated at 200-250°.

Higher Paraffins.

The number of pure aliphatic hydrocarbons which have been subjected to thermal decomposition is very limited. This seems strange, in view of the tremendous amount of study which has been directed to industrial cracking processes. From the theoretical considerations which have been developed earlier in the monograph, one may predict the course of pyrolysis for paraffin hydrocarbons, and, in the cases which are known, the experimental evidence coincides fairly well.

Propane.

Two types of decomposition for propane may be predicted on the basis of the methane system (p. 22). From its relationship to ethanol, which eliminates either hydrogen or water, propane should pyrolyze into propylene or ethylene by eliminating hydrogen or methane:

$$CH_3{-}CH_2{-}CH_3 \begin{cases} \nearrow & CH_3{-}CH{=}CH_2 + H_2 \\ \searrow & CH_2{=}CH_2 + CH_4 \end{cases}.$$

By assuming decomposition into radicals, there should be both C—C scission and C—H scission:

$$CH_3{-}CH_2{-}CH_3 \longrightarrow [CH_3{-}CH_2{-}] + [CH_3{-}] \longrightarrow CH_2{=}CH_2 + CH_4$$

or,

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \rightleftharpoons C_3H_4 + 2H_2 \longrightarrow 3C + 4H_2$$

From results with the simpler hydrocarbons, it may be inferred that two hydrogens at least must be eliminated for hydrogen to be evolved

[52] Dewar, *Compt. rend.* **84**, 611 (1877).
[53] Meyer and Sandmeyer, *Ber.* **16**, 2176 (1883).
[54] von Pechmann, *Ber.* **31**, 2950 (1898).
[55] Heinemann, French 458,397, 1913; German, 21,963; 22,647; Friedlaender, *Fortschritte der Teerfarben Fabrikation* (Julius Springer, Berlin) **11**, 829 (1915); **12**, 19 (1916); *Chem. Zentr.* **1921**, iv, 191; Houben-Weyl, "Die Methoden der Organischen Chemie," Leipzig, Georg Thieme **1922**, II, 601.
[56] R. Meyer, *Ber.* **45**, 1609 (1912); **46**, 3183 (1913); **47**, 2765 (1914); **50**, 422 (1917); **51**, 1571 (1918); **53**, 1261 (1920).
[57] Berthelot, *Compt. rend.* **127**, 908 (1898); **128**, 333 (1899); *Ann. chim. phys.* [7] **17**, 289 (1899).

as such. In other words, hexane would not be anticipated by the formation of, and the coupling of, two propyl radicals.

With propane of 97.5 percent purity, there is a 17.2 percent increase in volume as 250 cc. of it is maintained [58] at 650° for eleven seconds in a tube of 15.2 cc. capacity. The analysis of the final gaseous products reveals 58.6 percent of unchanged propane, 14 percent of methane, 7.5 percent of hydrogen, and 18.1 percent of unsaturated hydrocarbons and presumably a mixture of fairly large amounts each of ethylene and propylene. Pease finds that the pyrolysis of propane and also of the butanes is apparently a homogeneous gas reaction and monomolecular at the start.

Frey and Smith [33] have heated propane (99.0 percent purity) in a silica flask at 575°. The details are similar to those of their work with ethane. The course of the reaction may be followed by reference to the following table.

TABLE X. *Pyrolysis of Propane at 575° and 760 mm.*

Duration of heating, in minutes	Start	1	2	4	6
			Percent		
Propane	99.0	81.9	71.4	58.9	50.1
Propylene	...	4.4	6.8	9.1	10.7
Hydrogen	...	3.7	5.6	8.0	8.6
Methane	...	4.3	7.5	11.7	15.3
Ethylene	...	3.7	6.1	8.2	10.3
Ethane	...	0.8	1.4	3.2	3.8
Nitrogen	1.0	1.2	1.2	0.7	0.9
Higher hydrocarbons	...	...	...	0.3	0.4

These investigators believe that these data may be explained by two equations:

$$C_3H_8 \longrightarrow C_2H_4 + CH_4 \quad \text{and} \quad C_3H_8 \longrightarrow C_3H_6 + H_2,$$

which proceed at about equal rate, and a third equation of much lesser importance due to its slower reaction rate:

$$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4.$$

According to a recent patent,[59] propylene may be prepared from propane by subjecting the latter to "optimum thermal conditions". Pyrolysis of the ethane-propane fraction [60] of natural gas condensate gives ethylene and propylene as unsaturated hydrocarbons. These olefines, as well as butylene result by the action of heat on the propane-butane [61] fraction. In both cases, the percentage of unsaturated hydro-

[58] Pease, *see* Ref. 31.
[59] Haynes and Curme, Can. Pat. 245,154. *Chem. Abstracts* **19**, 657 (1925).
[60] Zanetti and Leslie, *Ind. Eng. Chem.* **8**, 777 (1916).
[61] Zanetti, *ibid.* **8**, 674 (1916).

carbons increases with increasing temperature up to 750°, above which it decreases. The formation of aromatic compounds begins at 750°, and is coincident with an increase in the rate of formation of carbon and hydrogen. In a study of the formation of aromatic hydrocarbons from the ethane-propane [62] fraction, it has been found that 850° is the optimum temperature for the formation of liquid tar when the gas is passed through a silica tube at the rate of 0.5 cu. ft. per hour (about 250 cc. per min.). About 10 cc. of the tar is formed per cu. ft. of gas. Most metals do not affect the formation of aromatic hydrocarbons, but nickel, iron and cobalt are effective anticatalysts since they promote a vigorous decomposition into carbon and hydrogen. An increase of pressure inhibits the tar formation. Decreasing the pressure produces more unsaturated bodies but less actual tar. One of the unsaturates is butadiene, the formation of which may possibly be traced through ethylene (p. 60). Davidson suggests that the mechanism for the formation of aromatic hydrocarbons is as follows: ethane → ethylene → butadiene → benzene; or more generally, paraffin → olefine → conjugated diolefine → aromatic hydrocarbon. Acetylene appears not to assist the formation of aromatic hydrocarbons from this ethane-propane fraction, at least in dilutions from 0.1 percent to 10 percent.

Isobutane.

From considerations of the "methane system", *iso*butane is comparable to *iso*propyl alcohol. Since the latter very largely pyrolyzes either into propylene and water or into acetone and hydrogen, it may be argued that *iso*butane should decompose according to two like reactions:

$$(CH_3)_2CH—CH_3 \longrightarrow CH_3—CH=CH_2 + CH_4,$$

or

$$(CH_3)_2CH—CH_3 \longrightarrow (CH_3)_2C=CH_2 + H_2.$$

The same conclusions are reached if an original scission into radicals is postulated.

At 500° and a rate of flow of about 230 cc. per minute, flowing downward through a vertical, electrically heated, 30-inch pyrex tube, *iso*butane [63] undergoes little or no decomposition. At 600° and a rate of flow of 346 cc. per minute, which represents a contact time of 36 seconds, 1000 cc. of this hydrocarbon changes into about 1150 cc. of

[62] Zanetti and Egloff, *ibid.* 9, 474 (1917); Davidson, *ibid.* 10, 901 (1918).

[63] Hurd and Spence, unpublished results. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

reaction products. The latter is about 75 percent unchanged *iso*butane. Of the one-quarter which is decomposed, about 90 percent undergoes pyrolysis according to the two reactions indicated above. From the 220 cc. of *iso*butane which appeared to undergo decomposition, the following gaseous products represent the experimental data; methane, 130 cc.; propylene, 63 cc.; *iso*butylene and hydrogen, 83 and 78 cc. respectively; ethylene, 13 cc.; acetylene, 5 cc.

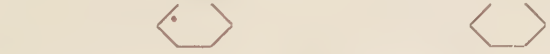
With approximately the same rate of flow (330 cc. per minute), there is 64 percent decomposition of the *iso*butane at 700°. The noticeable difference in the products of reaction is the greater amount of ethylene. As before, from 1000 cc. of *iso*butane, 640 cc. suffers pyrolysis; from the latter, there arises methane, 470 cc.; propylene, 238 cc.; *iso*butylene and hydrogen, 209 and 228 cc. respectively; ethylene, 115 cc.; and acetylene, 11 cc. As at 600°, therefore, these data indicate that the two reactions given above are still the major ones. However, the production of ethylene in quantity points strongly to a reaction of hydrogen with either propylene or *iso*butylene.

$$2H + CH_3{-}CH{=}CH_2 \longrightarrow CH_4 + CH_2{=}CH_2,$$

or

$$4H + (CH_3)_2C{=}CH_2 \longrightarrow 2CH_4 + CH_2{=}CH_2.$$

Such a reduction is similar to the high temperature reduction of toluene (p. 105) to methane and benzene. The equation brings out the similarity:



The effect of temperature on the decomposition, insofar as the relative quantities of olefines and hydrogen are concerned, is interesting. In these experiments, the rate of flow was rapid, between 800 and 1000 cc. per minute.

TABLE XI. *Effect of Temperature on Decomposition of* Isobutane *at a Rapid Rate of Flow.*

Temperature	500°	550°	600°	650°	700°
Percent olefines in the effluent gas	1.4	5.1	9.9	16.2	27.8
Percent hydrogen	0.5	1.3	2.0	5.8	10.7

Likewise, the effect of rate of flow on the relative quantities of olefines and hydrogen is instructive. Obviously, the effect of a slower rate of flow is to increase the contact time in the heated zone; therefore, the extent of pyrolysis should be greater, other things being equal.

TABLE XII. *Effect of Temperature on Decomposition of* Iso*butane at Slower Rates of Flow.*

Temperature °C.	Rate of Flow	300 cc/min.	400 cc/min.	800-1000 cc/min.
		Percent		
500	Olefines	6.9	...	1.4
	Hydrogen	1.3	...	0.5
600	Olefines	16.3	11.7	9.9
	Hydrogen	6.2	5.5	2.0
700	Olefines	34.6	32.1	27.1
	Hydrogen	15.8	12.9	11.7

At 750°, methane constitutes over half of the gas, and except for a little undecomposed *iso*butane, no other paraffins are present. Pease [58] reports the following gaseous mixture after heating *iso*butane (97.5 percent purity containing some propane) for eleven seconds at 650°; *iso*butane 44.5 percent; unsaturates 23.4 percent; methane 17.9 percent; hydrogen 12.8 percent; and nitrogen 1.3 percent. According to the conditions of the experiment (250 cc. of gas, and a heated bulb of 15.2 cc. capacity), there is about 25 percent increase in volume. A very interesting observation is that hydrogen is practically an inert diluent at 650°. Thus, a given volume of *iso*butane gives much the same volume of each gaseous product, whether or not it is initially diluted with half of its own volume of hydrogen. This was found to be true with *n*-butane as well. As reported earlier (p. 65), the pyrolysis of the butanes seems to be a homogeneous gas reaction, and monomolecular at the start.

N-BUTANE.

Pease's experiments with *n*-butane (97.5 percent purity containing some pentane) were similar to his experiments with ethane, propane and *iso*butane. At 650°, after ten seconds' time, there is about a 35 percent increase in volume and the final gases, by volume, are as follows: butane 43 percent; methane 24.5 percent; unsaturates 26.3 percent; hydrogen 4.5 percent. Nitrogen or hydrogen may be added before the pyrolysis, with very little ultimate change in the products.

Experiments have been performed recently by Hurd and Spence [64] which indicate that at 600° and a contact time of about one minute, two equations account for the greater part of the reaction products:

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3{-}CH{=}CH_2,$$

and

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2.$$

[64] Hurd and Spence, unpublished results.

The extent of the decomposition of the *n*-butane is about 20 percent under these conditions (temperature of 600°; rate of flow of 336 cc. per minute; same procedure as with isobutane), and the first reaction into propylene appears to proceed more rapidly than the second which gives ethylene. At 700° and a similar rate of flow (315 cc. per min.), there is 75 percent decomposition, and the growth of the ethylene content, at the expense of propylene, is interesting.

$CH_3CH_2CH_2CH_3 \longrightarrow$	$CH_4 + CH_3{-}CH{=}CH_2$	44 percent
$\longrightarrow$	$CH_3CH_3 + CH_2{=}CH_2$	46 percent
$\longrightarrow$	H_2 + butenes	5 percent
$\longrightarrow$	$2H_2 + CH_2{=}CH{-}CH{=}CH_2$	4 percent

n-Butane, in the 600° experiment (contact time, 35 seconds), was found to undergo a 15 per cent increase in volume; and in the 700° run (contact time, 28 seconds), an 87 percent increase. From the data of these results, it may be shown that 1000 cc. of *n*-butane gives 1155 cc. of gaseous products at 600°, of which the composition is as follows: olefines, 173 cc. (propylene 91 cc.; ethylene 73 cc.; higher olefines and dienes 9 cc.); hydrogen, 24 cc.; methane, 80 cc.; ethane, 65 cc.; butane, 813 cc. Similarly, at 700°, there is a volume change of 1000 cc. to 1870 cc., of which the composition is as follows: olefines, 721 cc. (propylene 304 cc.; ethylene 356 cc.; higher olefines and dienes 61 cc.); hydrogen, 159 cc.; methane, 312 cc.; ethane, 370 cc.; butane, 308 cc.

Other work on the pyrolysis of butane has been done by Zanetti,[61] on the propane-butane fraction of natural gas condensate. Since the butane content was 3-16 percent of the total, no definite conclusions relative to the pyrolysis of butane can be drawn from this work. It may be added that ethylene predominated in the olefines, and that fairly large amounts of benzene were formed at a temperature of 500-1000°. The latter fact again demonstrates that aromatic hydrocarbons may be formed from paraffins with less than six carbons in the molecule.

The Pentanes.

According to the methane system, *n*-pentane should behave as a methano-alcohol or as a methano-ester; thus, the functional groups would be $R{-}CH_3$ or $R{-}CH_2{-}R$. Prediction on this basis (see p. 23) would lead to the formation of methane + butene; ethane + propene; or hydrogen + pentene. *Iso*pentane should break at the branched carbon if the assumptions underlying the methane system are correct. From the viewpoint of electron attraction of radicals, the conclusions are similar. These have been developed on p. 29.

Norton and Andrews [65] heated *n*-pentane at "red heat" and obtained large amounts of propylene and ethylene, and also a large volume of saturated hydrocarbons. In an endeavor to locate an industrial outlet for the lower boiling fraction of petroleum ether, Calingaert [66] studied the behavior of *n*- and *iso*pentane at 600°. No satisfactory preparation of C_4 or C_5 unsaturated hydrocarbons was found, but the results are of great theoretical interest. The unsaturated hydrocarbons from the reaction were absorbed in bromine and water, after which the saturated gases were condensed by liquid air. Distillation of this condensate in the vacuum of a mercury vapor pump gave a first fraction containing hydrogen and methane. Each succeeding fraction contained no more than two hydrocarbons and was analyzed by explosion with oxygen in the usual way.

With a rate of flow of one-sixth mol per hour, only 30 percent of the original pentane decomposes. Of this portion, 55 percent of *n*-pentane pyrolyzes into ethane and propylene, 25 percent into propane and ethylene, and the largest part of the remaining 20 percent into methane and butylene. Some hydrogen also appears. With *iso*pentane, 90 percent of the decomposition product is either methane and the two *n*-butylenes, or ethane and propylene, the former predominating. These results indicate that the smaller group is the one most liable to become saturated at the expense of the other, especially so if one of the groups is branched. The behavior of the *n*-propyl residue and the *iso*propyl residue towards an ethyl group is instructive, and shows that the methods of thermal decomposition may form an independent method of determining the relative electron attraction of radicals (see p. 28). In the two cases below,

(a) $CH_3—CH_2—CH_2— + —CH_2—CH_3$
(b) $(CH_3)_2CH— + —CH_2—CH_3$,

the propyl radical in (a) not only gives but loses hydrogen, since both propylene and propane are formed, but in (b), it seems that the *iso*propyl group is incapable of grasping a hydrogen from ethyl for propane was never observed. Neither was *iso*butane found. Small amounts of a pentylene and hydrogen also come from *iso*pentane, and by secondary reactions butadiene and *iso*prene.

Hexane.

The methane system would predict scission (by heating) at all three places in the *n*-hexane chain, and it would also predict hydrogen evolu-

[65] Norton and Andrews, *Am. Chem. J.* **8**, 1 (1886).
[66] Calingaert, *J. Am. Chem. Soc.* **45**, 130 (1923).

tion. With the higher normal paraffins, therefore, the value of the methane system diminishes since no preference is indicated for the various possibilities. The theory of radical electron attraction offers more promise but here one is hampered by conflicting data regarding the relative electronegativity of the various alkyl groups. Possibly the methods of pyrolysis must eventually supply the scale of electron attraction, but thus far too few pure paraffins have been subjected to critical pyrolytic experiments. If the series "methyl > ethyl > propyl > butyl > pentyl" is accepted, then scission of the C_6 chain into $C_3 + C_3$ or $C_4 + C_2$ should predominate, with $C_5 + C_1$ a rather minor primary reaction.

Haber's results with *n*-hexane are the most thorough to date although it has been studied rather extensively by other workers. For example, at "red heat" with a slow rate of flow (about 25 cc. per hour), Norton and Andrews [65] obtained nearly equal amounts of ethylene and propylene, both in large amounts, and large amounts of saturated gases. About 12 percent of the hexane was recovered. Small amounts of benzene, butadiene, amylene and hexylene also appeared. Acetylene was absent. At a lower temperature, 700°, neither benzene nor ethylene was formed, although propylene was formed in quantity. They found the lowest decomposition temperature in this type of experiment to be about 600°. According to Worstall and Burwell,[67] at 600° *n*-hexane decomposes chiefly into methane, ethylene and propylene. These olefines were considered to come from amylene. At 1200°, hexane decomposes into its elements. For the synthesis of acetylene from hexane in the electric arc, see p. 52.

Haber [68] considered that his results with *n*-hexane at 600° were best interpreted on the basis of a primary decomposition into methane and amylene. However, his data show that the chief unsaturated reaction product is propylene and not amylene. Therefore, without proof to the contrary one may question Haber's assertion that the amylene decomposed at once into propylene and ethylene. It seems reasonable to infer that the propylene was formed as a primary product.

The location of the lowest temperature of decomposition for *n*-hexane depends not only on the duration of heating but also on the pressure, and of course on the presence of catalysts. It is not altered by limiting heating (Haber) at 518°, but it decomposes almost explosively [69] at this temperature under high pressure. Cyclohexane is more stable, and benzene is much more stable (see p. 88).

[67] Worstall and Burwell, *Am. Chem. J.* **19**, 815 (1897).
[68] Haber, *Ber.* **29**, 2694 (1896); *J. Gas Lighting*, **68**, 367, 458, 501 (1896).
[69] Ipatiew and Dowgelewitsch, *Ber.* **44**, 2987 (1911).

From 61 grams of *n*-hexane [70] at 606° there results 0.32 gram of hydrogen, 36.5 grams of olefines, 11.4 grams of paraffins at least 70 percent of which is methane, and 3 grams of benzene. There is no more than a trace of carbon and acetylene. Of the olefines, 6 grams is liquid (amylene), and 30.5 grams gaseous with a molecular weight of 39, therefore largely propylene (the molecular weight of ethylene is 28, and of propylene is 42). Similar results come at 730° and at 820°, but at 1190-1220° the decomposition is largely to carbon and hydrogen. Haber and Oechelhäuser [71] showed that as much benzene formation is apparent from *n*-hexane at 600° as at 900°. Between 900-1000°, hexane yields 27.77 percent methane, 22.14 percent olefines, 1.1 percent acetylene, 3.27 percent carbon, 2.44 percent hydrogen, 6.7-10 percent benzene, traces of naphthalene, and 29.22 percent tar.

Norton and Andrews [72] reported large amounts of ethylene, propylene and saturated gases from the pyrolysis of *isohexane* at red heat. Moderate amounts of butylene, and small amounts or traces of butadiene, benzene and amylene also were noted.

Heptane and Octane.

The literature dealing with the pyrolysis of higher hydrocarbons is very scanty. Crude *heptane* and *octane* were pyrolyzed [73] at 900° in a commercial oil-gas plant. This consisted of an iron pipe, 40 feet long, into which the liquid was added at one end drop by drop. In such an apparatus, the hydrocarbon yields a small deposit of very hard carbon, and also forms tar (25 percent by weight of the original oil), liquid (10 percent) formed by compression of the gas, and the gas itself. The liquid is four-fifths benzene and one-tenth toluene and xylene. It contains 6 percent of unsaturated hydrocarbons (boiling point 20-78°), and 4 percent of gases boiling below 20°. The tar is 34 percent benzene and toluene in a ratio of 3:2, 14 percent xylenes, 11.7 percent naphthalene, 14.2 percent oils, 2.3 percent anthracene and 21 percent of higher boiling material and tarry residue. A small amount of heptane and octane may be found in the benzene and toluene distillates, but no lower paraffins. Two-thirds of the gas is a hydrogen-methane mixture with a volume ratio of 1:3. The remainder consists of unsaturated hydrocarbons, without higher paraffins.

[70] Haber and Samoylowicz, *Chem. Zentr.* **1896** (2), 377.
[71] Haber and Oechelhäuser, *Chem. Zentr.* **1897** (1) 225.
[72] Norton and Andrews, *Am. Chem. J.* **8**, 8 (1886).
[73] Worstall and Burwell, *Am. Chem. J.*, **19**, 815-845 (1897). This gives a good summary of previous work on the thermal decomposition of hydrocarbons.

HEXAMETHYL ETHANE.

Very recently, the behavior of *hexamethyl ethane*[74] at high temperature has been investigated. Preliminary results seem to indicate less than 2 percent of decomposition at 450° as the vapors of this octane are passed through an empty Pyrex tube about a foot long. At 500°, the volume of gas which is formed corresponds to 17.3 percent cracking; at 535°, 53 percent; and at 550-570° it is completely decomposed. At this point, 0.001 mol of hexamethylethane yields very nearly three volumes of gas (59 cc. instead of 67.2 cc.). As yet the gases have not been investigated, but their volume indicates a probable pyrolysis into equimolecular amounts of methane, propylene and *iso*butylene:

$$C_8H_{18} \longrightarrow CH_4 + C_3H_6 + C_4H_8.$$

The mechanism has already been discussed on pp. 30-31.

Conant has also performed similar experiments with *n*-octane. The results indicate that this is more stable than its branched-chain isomer. At 450° there is no cracking; at 480-500°, about 4 percent; at 560°, 22 percent; and at 630°, 0.001 mol yields 66 cc. of gas (at a temperature of 0° and a pressure of 760 mm.). The temperature necessary for about 50 percent decomposition of hexamethyl ethane is approximately 525°, and of *n*-octane is about 580°.

The fact that hexamethyl ethane pyrolyzes more readily than *n*-octane may have a bearing on anti-knock studies. In a discussion of lead tetraethyl, Taylor[75] suggests that not only may lead atoms function (see p. 729) as oxidation centers in oxygen-hydrocarbon mixtures, but also, and to a much more marked extent, the free radicals (such as Et from $PbEt_4$, by pyrolysis) may function as oxidation centers. If this is true, it helps us to visualize why branched paraffins knock less than their straight-chain isomers. The former, on heating, undergo scission more readily into radicals.

HEXADECANE.

Gault[76] and coworkers have approached the problem of cracking by studying the behavior of a pure hydrocarbon, hexadecane, under varying conditions of temperature and pressure. Tubes, either glazed porcelain or quartz, 16, 32, 48 and 64 cm. long were heated in an electric furnace in 70° steps from 390-815°. Below 390°, decomposition was inappreciable. The following factors were found to vary directly with

[74] Conant and W. C. Mendum, Harvard University; private communication, 1927.
[75] Taylor, *Nature* **119**, 746 (1927); *Chem. Abstracts* **21**, 2555 (1927).
[76] Gault and Hessel, *Compt. rend.* **179**, 171 (1924); *Ann. chim.* [10] **2**, 319-377 (1924). Gault and Bargmann, *Ann. off. nat. comb. liq.* **1**, 77-142 (1926); *Chimie & industrie* **16**, 242 (1926). Gault and Sigwalt, *Chem. Abstracts* **22**, 379 (1928).

the temperature and the length of the tube, but inversely with the rate of flow (1/3, 1, and 2 cc. of the liquid per minute) of the hexadecane.

(a) *Volume of Gaseous Products.* Each 100 grams of hexadecane produces 20 liters of gas at 640° and 50 liters at 800° (64 cm. furnace, and rate of flow of 1 cc. per min.). The quantity of gas at 500-600° increases with the pressure up to 3 kg./cm², and then remains constant to 9 kg./cm².

(b) *Hydrogen Output.* Hydrogen is just detectable at 540°; at 615° its volume is 14 percent of the gas; and at 800°, 23 percent (64 cm. furnace and other conditions as before). For this, the following equation is assumed: $R—(CH_2)_4—R' \rightarrow R—CH=CH_2 + CH_2=CHR' + H_2$. The hydrogen which is produced above 685° is thought to be largely due to the dehydrogenation of the naphthenes. The observed fact that the ratio of C_nH_{2n+2} to C_nH_{2n} changes in favor of the saturated hydrocarbons with increasing pressure is one which would be anticipated.

(c) *Percentage of Saturated Hydrocarbons in the Gas.* At 600° and at 800° the values respectively are 36 percent and 52 percent in the 64 cm. furnace, and 30 percent and 37 percent in the 16 cm. furnace, both at a rate of flow of 1 cc. per minute. At 470° and 570° the saturated hydrocarbons in the gas drop from 70 percent to 35 percent while the unsaturated rise from 28 percent to 55 percent. Gault and Hessel state that at 470°, the preponderating reaction is to ethylene and liquid paraffins, accompanied by a lesser pyrolysis into methane and liquid olefines. Under the influence of heat the olefines are transformed into naphthenes.

If preliminary scission into radicals (p. 26) is assumed, the latter reaction is well in keeping with the theory:

$$C_{16}H_{34} \longrightarrow [CH_3— + C_{15}H_{31}—] \longrightarrow CH_4 + C_{15}H_{30}.$$

Methyl is far more electronegative than hexadecyl, and presumably more so than pentadecyl; therefore, methyl attaches a hydrogen to form methane. However, in the scission of hexadecane into ethyl and tetradecyl, a change into ethylene and a paraffin (tetradecane) would indicate that ethyl is the less electronegative. However, this cannot be taken as proof, for tetradecane was not identified as such, nor was it established that ethylene was formed directly from the hexadecane. Gault and Sigwalt state that in the absence of catalysts, the chain of hexadecane appears to break indifferently at any point, but the positions of scission tend to approach the ends of the chain as the cracking

temperature increases. They state that the smaller compound formed by cracking is usually the olefine.

(d) *Refractive Index of the Liquid Product.* The value for pure hexadecane at 20° is 1.436; it changed from this to about 1.5 (at 800° in the 64 cm. furnace). Gault and Hessel believe that these results, together with those of the iodine number (below) point to the conclusion that the terminal dissociation of the hydrocarbon predominates.

(e) *Density of the Liquid.* The density (D_4^{20}) is 0.776 for pure hexadecane. The density of the liquid from the 64 cm. furnace exceeds 0.880. Graphical analysis of the data shows vividly that the variations in density are of exactly the same type as the variations in the refractive index.

(f) *Formation of Aromatics.* This is revealed by the solubility of the liquid products in dimethyl sulfate.[77] The aromatic formation starts at 685°. The liquids consist of saturated, unsaturated, acyclic and cyclic hydrocarbons, and pressure favors both cyclization and hydrogenation.

(g) *Iodine Number of the Liquid, Below 700°.* The change is a gradual one from 12 at 500° to 46 at 700°. A break in the curve appears at 700° for the long furnaces and about 750° for the shorter ones and the iodine numbers diminish thereafter with increasing temperature.

(h) *Percentage of Liquid with a Lower Boiling Point Than Hexadecane* (284-290°). This change is from about 2 percent at 500° to 54 percent at 800°.

The reverse relations were found to hold for:

(a) *Percentage of Unsaturated Hydrocarbons in the Gas Above 540°.* At 540° in the 64 cm. furnace (1 cc. per min.) about 55 percent is present, and this value drops to 26 percent at 800°. In the 16 cm. furnace, the value drops from 69 percent at 610° to 55 percent at 800°. The values for the 32 and 48 cm. furnaces fall regularly between these.

(b) *The quantity of Liquid Product Obtained.*

(c) *Iodine Number of the Liquid Above 750°.*

Gault and Bargmann's results indicate the value of pressure in the decompositions, a result which is confirmed in practice.

Unsaturated Hydrocarbons.

The methane system of compounds (p. 23) classifies ethylene as "methano-formaldehyde", and homologous α-olefines as "methano-acids" or methano-esters. Details for the pyrolysis of ethylene have already been given. With other olefines, the methane system leads to

[77] Valenta, *Chem. Ztg.* **30**, 266 (1906).

the conclusion that the single bond is broken more readily by heat than the double bond. The case of carbon monoxide diethyl acetal, $(C_2H_5O)_2C$, is not an exception to this statement. This is the bivalent carbon compound which Scheibler [78] isolated instead of its dimer, $(C_2H_5O)_2C{=}C(OC_2H_5)_2$. Although attempts to prepare the latter resulted in spontaneous scission at the double bond, it is evident that this substance resembles ethylene in having no single carbon-to-carbon linkage attached directly to the ethylene chain.

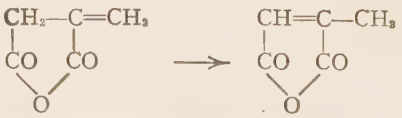
Electron Attraction of Unsaturated Radicals.

The vinyl radical, $CH_2{=}CH{-}$, has not been mentioned in the earlier chapter (p. 26) on electron attraction, but undoubtedly it is highly electronegative, probably much the same as phenyl. Vinyl chloride and phenyl chloride are very similar in properties, and both possess similar unsaturation; $H_2C{=}CH{-}Cl$ and $HC{=}C{-}Cl$. The allyl group, , $CH_2{=}CH{-}CH_2{-}$, on the contrary possesses but a slight degree of electron attraction. This is but another way of saying that the vinyl group is very firmly tied to such atoms as carbon, oxygen, sulfur, nitrogen, whereas the allyl group is less firmly attached. Therefore, in the chain $\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{CH_2}{-}\underset{4}{CH_2}{-}\underset{5}{CH_2}{-}$, scission between atoms 3 and 4 should predominate over 2 and 3.

Such speculations as these assume the constancy of the double bond in its original position in the molecule. It is doubtful whether or not this is always the case since rearrangements are known to occur in many cases at fairly low temperatures. One illustration occurring at 130° is the following: [79]

$$p\text{-}Br{-}C_6H_4{-}CH_2{-}CH{=}CH_2 \longrightarrow p\text{-}Br{-}C_6H_4{-}CH{=}CH{-}CH_3.$$

Another is the conversion of itaconic anhydride to citraconic anhydride [80] by ordinary distillation:



Both of these illustrations reveal a tendency towards the formation of a conjugated system.

[78] Scheibler, *Ber.* **59**, 1022 (1926).
[79] Quelet, *Compt. rend.* **182**, 1283 (1926).
[80] Fittig, *Ann.* **304**, 122 (1899).

In this connection it may be noted that the purity of many of the simple and supposedly pure α-olefines in the literature has recently been challenged, because of the development of synthetic methods [81] for this type of compound which leaves scarcely any doubt as to the position of the double bond. It is of interest to note that undecylenic acid, $CH_2=CH-(CH_2)_8CO_2H$, which is prepared pyrolytically, possesses α-unsaturation and is of unquestioned structure (see p. 164).

Propylene.

Propylene [82] is stable at 550°, but at 350° over nickel it decomposes into a mixture [83] of ethylene, methane, ethane and propane. Rather careful experiments with propylene [84] have shown that it undergoes almost negligible pyrolysis at temperatures up to 525° (rate of flow of 450 cc. per min. through a 2-ft. length of pyrex combustion tube). Fifty degrees higher, however, pyrolysis sets in, and if propylene [85] is heated for four minutes at this temperature (575°) in a 400 cc. transparent silica flask, the following gaseous products arise; unused propylene, 68.9 percent; methane, 10.7 percent; ethylene, 8.0 percent; propane, 3.0 percent; butylene, 2.8 percent; higher hydrocarbons, 2.6 percent; ethane, 1.9 percent; hydrogen, 1.7 percent; nitrogen, 0.4 percent; acetylenes, none. By taking a gaseous mixture of propylene and hydrogen and heating it in the same way for measured durations of time at 575°, it is found that methane and other hydrocarbons are gradually formed. The following data indicate this behavior:

Table XIII. *Pyrolysis of Propylene.*

Duration of heating, in minutes	Start	1	2	6
		Percent		
Propylene	43.7	40.1	37.7	25.0
Hydrogen	54.7	53.0	49.4	49.9
Ethylene	0.3	1.6	2.7	6.1
Methane	...	1.8	4.2	9.4
Ethane	...	0.4	1.2	1.9
Propane	0.6	1.2	1.8	4.3
Higher hydrocarbons	...	1.4	2.4	2.4

The reactions:

$$C_3H_6 + H_2 \longrightarrow C_3H_8,$$

and

$$C_3H_6 + H_2 \longrightarrow C_2H_4 + CH_4$$

[81] Boord, Detroit meeting of the American Chemical Society, 1927; *also* Borgueul, *Bull. soc. chim.* **41**, 1475 (1927).
[82] Berthelot, *Compt. rend.* **129**, 490 (1899).
[83] Sabatier and Senderens, *ibid.* **134**, 1127 (1902).
[84] Hurd and Spence, unpublished results.
[85] Frey and Smith, private communication, 1928; published by permission of the Director of the Bureau of Mines.

may be considered as concurrent ones here, and it is interesting to note that the latter reaction proceeds more rapidly. Furthermore, ethylene and methane appear to be formed nearly as rapidly from propylene alone as from the mixture of propylene and hydrogen. The hydrogenation of ethylene at 575° in silica vessels was found to be much faster than that of propylene under the same conditions; furthermore, under these conditions, the hydrogenation of ethylene into ethane takes place considerably faster than the reverse process of dehydrogenation.

Butylene.

Butene-1, prepared by the dehydration of *n*-butyl alcohol [86] with a neutral catalyst, undergoes pyrolysis at 600°. Acetylenes are never formed, but the products are propylene, methane, butadiene and hydrogen. The presence of methane indicates the possibility that allene might be an unidentified product of the reaction:

$$CH_3—CH_2—CH=CH_2 \longrightarrow CH_4 + CH_2=C=CH_2,$$

but Calingaert [87] thinks the presence of methane in the products of cracking cannot be explained by a simple equation. He reasons that since methane is the most stable paraffin hydrocarbon in the temperature range in which the experiments are performed, it is not surprising that a large percentage of it is always formed, almost regardless of the nature of the initial products.

The fact that butadiene may be formed by heating butene-1 has been mentioned in a patent. In the specifications,[88] 100 grams of it is passed during one hour through a red hot tube, 3 ft. long, containing metallic copper. Therein also it is mentioned that other related dienes may be prepared by the thermal decomposition of olefines with the structure, $=C=C—CH—CH—$.

Isobutylene.

From a theoretical standpoint, *iso*butylene is of great interest since it should yield allene as a product of thermal decomposition (p. 25). With alumina or graphite as catalysts,[89] *iso*butylene gives rise to hydrogen, 15.8 percent; paraffins, 14.2 percent; and about 70 percent of unsaturated hydrocarbons. At 70 atmospheres pressure and a temperature of 380-400°, *iso*butylene polymerizes into paraffins, olefines, cycloparaffins, etc.

[86] Calingaert, *J. Am. Chem. Soc.* **45**, 134 (1923).
[87] Calingaert, private communication, 1927.
[88] Perkin, Weizmann, Mathews and Strange, Brit. Pat. 9722, 1911.
[89] Ipatiew, *Ber.* **36**, 2003 (1903); **37**, 2961 (1904).

When *iso*butylene [90] is slowly passed through a 60 cm. glass tube, heated to low redness, there is a considerable tendency towards the formation of aromatics (25 cc. of condensed liquid from an unstated volume of olefine), which include about equal amounts of benzene and toluene (4 grams of each) and a considerable quantity of naphthalene. Ethylene, propylene, unused *iso*butylene and butadiene-1,3 comprise the olefines identified from 200 grams of olefine bromides of the reaction. Noyes believed that the pronounced formation of aromatics was due to the butadiene. The unabsorbed gases are only hydrogen and methane. Styrene was not definitely identified, and acetylene was shown to be absent.

Noyes worked with both ethylene and *iso*butylene, and he found the latter to undergo pyrolysis much more easily. It is not clear how *iso*butylene, a branched compound, can change into butadiene, a straight chain compound with the same number of carbon atoms, by any simple mechanism. Recent work by Norris and Reuter on the pyrolysis of trimethylethylene (see below, Reference 93) is interesting in this connection, although it does not provide an answer to the question. *Iso*butylene is regarded as one of the products formed when this pentylene is thermally decomposed, but the presence of butadiene could not be demonstrated. Nef [91] reported that *iso*butylene starts to decompose at 570° (over pumice) into methane, hydrogen, propylene and some carbon (see p. 127). Nef did not use pure *iso*butylene at the outset, but his *iso*butylene was formed as a pyrolytic product of tertiary butyl chloride. This, of course, may influence the result.

Recent work with *iso*butylene in the author's laboratory [92] reveals the fact that it suffers only about 1 percent pyrolysis at 600° with a hot contact time of 21 seconds. The decomposition is only 20 percent when the contact time is extended to 4 minutes. It is apparent, therefore, that *iso*butylene is more stable than *iso*butane (p. 67), since the latter is nearly 25 percent decomposed at 600° in a contact time of 36 seconds. The greater thermostability of *iso*butylene affords an excellent opportunity for an explanation using the postulate of electron attraction; namely, that scission of a hydrocarbon by heat tends to produce radicals of low electron attraction. Since there is every reason to believe that the double bond is a position of strength insofar as carbon-to-carbon scission is concerned, obviously scission of the carbon chain in *iso*butylene must produce the radicals, CH_3— and CH_3—$\underset{|}{C}$=CH_2 (a

[90] Noyes, *Technology Quarterly* **1**, 278-281 (1888).
[91] Nef, *Ann.* **318**, 22 (1901).
[92] Hurd and Spence, unpublished data.

substituted vinyl), whereas scission of the carbon chain in *iso*butane must produce CH_3— and CH_3—$\underset{|}{CH}$—CH_3 (a secondary alkyl). Methyl is the same in both cases. However, the substituted vinyl group (from *iso*butylene) should exert a high electron attraction (p. 76), whereas the secondary propyl group (from *iso*butane) should exert a much lower attraction (p. 27). Thus, isobutane would be less stable than isobutylene; as stated above, this corresponds to fact.

In the experiment cited (600°, and contact time of 200 seconds), the following gaseous products are produced from each liter of *iso*butylene: methane 118 cc.; *iso*butane 54 cc.; propylene 61 cc.; acetylene 3 cc.; ethylene (and aromatic vapors) 18 cc.; hydrogen 35 cc. The unused *iso*butylene is also present. Also, there is formed about 0.5 gram of an oil; this represents about a 20 percent of liquid condensate.

The contact time is calculated by dividing the volume of the reaction tube by the mean rate of flow of gas per second through the tube, this mean volume being corrected to the temperature of the reaction tube.

At 700°, with a contact time of 18 seconds, the decomposition of *iso*butylene proceeds to the extent of 48 percent, and the yield of liquid hydrocarbons is about 30 percent by weight of the *iso*butylene used. In several experiments with contact times varying from 18 to 32 seconds, the percentage of this oil fluctuated between 20 and 30 percent. One liter of *iso*butylene yields 1175 cc. of gaseous products, including unchanged *iso*butylene. The products of decomposition follow: methane 312 cc.; *iso*butane 29 cc.; propylene 109 cc.; acetylene 28 cc.; ethylene (and aromatic vapors) 32 cc.; hydrogen 124 cc. There is no butadiene, contrary to the work of A. A. Noyes. The quantity of oil formed simultaneously with the 1175 cc. of gas is about 0.8 gram. Benzene and toluene comprise somewhat more than half of this oil; the remainder appears to consist of xylene, naphthalene, methyl naphthalene, diphenyl, anthracene, phenanthrene.

The rate of disappearance of the *iso*butylene is unchanged by dilution of the entering gas with nitrogen or with hydrogen. The rate of decomposition is, therefore, independent of the concentration. It may be noted that hydrogen is not an inert diluent at this temperature (700°), since much of it disappears. The rate of decomposition of the *iso*butylene is also independent of the surface in the reaction tube, as was proved by packing the tube with small pyrex tubing. The decomposition is therefore homogeneous, or largely so.

Since the decomposition of *iso*butylene is independent of the concentration, and is not affected by an increase of surface, the reaction

is unimolecular, and the rate of decomposition should be represented by the equation:

$$\frac{dx}{dt} = k\,(a - x),$$

wherein k, on integration, becomes

$$k = \frac{1}{t} \log_e \frac{x}{(a - x)}$$

In these formulas, a represents the original concentration of the *iso*-butylene; $(a - x)$ is the concentration remaining after t seconds; and k is the specific reaction rate. In the calculation of the following values of k, the concentrations of *iso*butylene have been expressed in mols per 22.4 liters at 0°, 760 mm., and the time is expressed in seconds.

The final concentrations are somewhat in error, since the liquid products were removed before measuring the volume of the exit gases; therefore, the concentration of the *iso*butylene at the end of the reaction is actually less than the figures given in the following table.

Temperature °C.	Time Sec.	Concn. in Mols per 22.4 Liters Start	Finish	k	Mean k
600	200	0.940	0.690	0.0016	0.0016
650	13	.990	.900	.0073	
650	27	.970	.762	.0089	.0081
700	12	.980	.634	.0362	
700	18	.975	.433	.0451	
700	22	.978	.294	.0547	
700	23	.980	.387	.0405	
700	25	.978	.380	.0378	
700	32	.983	.266	.0409	
700 + N_2	21	.548	.212	.0451	
700 + H_2	22	.518	.206	.0420	
700 + pyrex surface	21	.978	.399	.0428	.043

The heat of activation may be calculated from the change in the specific reaction rate, by means of the equation of Arrhenius:

$$\frac{d(\log_e k)}{dT} = \frac{A}{RT^2},$$

wherein k is the specific reaction rate; T is the absolute temperature; R the gas constant in calories; and A the heat of activation. The mean values of k for the temperatures 600, 650 and 700° C. are used here.

Mean Temperature	Heat of Activation, A
625° C.	52,700 cal. per mole.
650	55,700
675	59,100

PENTYLENES.

Trimethylethylene is the most stable of the isomeric pentylenes, and *iso*propylethylene apparently the least. Trimethylethylene [93] does not rearrange into any of the other forms, and the same may be said for pentene-2. However, about one-third of *iso*propylethylene rearranges into trimethylethylene by passing it through a 4 ft. silica tube at 515°, but below 450° (without catalysts) there is no rearrangement. This process adjusts the double bond into a more symmetrical arrangement:

$$CH_3CH(CH_3)-CH=CH_2 \longrightarrow CH_3C(CH_3)=CHCH_3 .$$

Aluminum sulfate appears to be a fairly effective catalyst for this rearrangement. At 555°, *iso*propylethylene not only rearranges but also pyrolyzes into smaller hydrocarbons. Ipatiew's data [94] indicate that this conversion proceeds to the extent of 80 percent at 525-535° in the presence of alumina, but that *iso*propylethylene is not appreciably changed by passing it through an empty glass tube at 500-550°. It is in keeping with these facts to record that *iso*amyl bromide,[95] when passed over lime at 400-500°, yields trimethylethylene and not *iso*propylethylene. Norris and Reuter observed a similar behavior in the dehydration of *iso*amyl alcohol.

A migration of the double bond, such as was observed in the case of *iso*propylethylene, is apparent in the case which follows. Here, however, the 4-bromo-1-allyl-benzene rearranges [79] at a low temperature, 130°:

$$Br-C_6H_4-CH_2-CH=CH_2 \longrightarrow Br-C_6H_4-CH=CH-CH_3 .$$

Two experiments with *pentene-2* are interesting (Norris and Reuter). In one, about one-third of the olefine is decomposed by heating at 575° for about 12 seconds, and in the other about two-thirds is decomposed at 600° for 15 seconds. The input rates, respectively, are 2 and 1.4 mols per hour. In the first, less than a 0.5 percent yield of butadiene is formed (less than 0.01 mol from 1.9 mols of the pentene), but in the second, there is about a 10 percent (molar) conversion. Thus:

$$CH_3CH=CHCH_2CH_3 \longrightarrow CH_2=CHCH=CH_2 + CH_4 .$$

The saturated gas from the latter experiment amounts to about half of the total gas, and is almost entirely methane. For every three mols of methane, there is one of butadiene. To summarize: for each mol of original pentene-2, 1 percent of a mol of methane results in the first

[93] Norris and Reuter, *J. Am. Chem. Soc.* **49**, 2624 (1927).
[94] Ipatiew, *Ber.* **36**, 2004 (1903).
[95] Nef, *Ann.* **318**, 28 (1901).

case and 34 percent in the second; of ethylene, 0.5 and 5.0 percent respectively; of propylene, 10 percent and 6-13 percent respectively; of hexylenes, 0.0 and 3 percent respectively; and of butadiene, 0.3 percent and 9-13 percent respectively.

Similar experiments with *trimethylethylene* give no positive evidence of the formation of *dienes*. The greater stability of trimethylethylene is apparent from the fact that it gives about the same amount of decomposition at 650°, for a 13 second exposure, as does pentene-2 at 600°. In this case also, methane is the only paraffin hydrocarbon (46 percent of a mol per mol of trimethylethylene), and it represents about half of the total volume of gas. About 4.7 molar percent of ethylene is formed, and (as with pentene-2) the percentage of propylene is greater than that of ethylene. Nef [96] had previously reported that methane (79.9 percent) and hydrogen (20.1 percent) constitute the gaseous portion from trimethylethylene over pumice at 590°, which is unabsorbed by bromine.

These results with pentene-2 and trimethylethylene indicate that it is more difficult to break the bond between a methyl radical and an unsaturated atom than between the radical and a saturated atom. Thus, the reaction:

$$CH_3CH_2CH{=}CHCH_3 \longrightarrow CH_3{-} + {-}CH_2CH{=}CHCH_3$$

proceeds more easily than either of the following two:

$$CH_3C(CH_3){=}CHCH_3 \begin{cases} \longrightarrow CH_3{-} + CH_3C(CH_3){=}CHCH_3 \\ \longrightarrow CH_3{-} + (CH_3)_2C{=}CH{-} \end{cases}$$

This, of course, is but another way of saying that the electron attraction of the substituted vinyl group is greater than the electron attraction of the substituted allyl group. This has been pointed out in detail in Chapter 2.

At 750°, isoprene is an important pyrolytic product [97] of trimethyl ethylene. This substance may be isolated by heating the amylene at reduced pressure and it undoubtedly plays an important rôle (see p. 60) in the formation of the aromatic hydrocarbons which are formed when the pyrolysis is conducted at atmospheric pressure. In these experiments the amylene is admitted to the hot tube at a rate of 15-17 grams per hour. At 15 mm., from 33 grams of decomposed amylene (50 grams less 17 grams recovered), 8 grams of isoprene is formed. A considerably smaller amount of butadiene also appears. Without the

[96] Nef, *Ann.* **318**, 219 (1901).
[97] Staudinger, Endle and Herold, *Ber.* **46**, 2475 (1913).

vacuum, 50 grams of amylene produces 14.5 grams of liquids, chiefly aromatic, boiling above 80°, and only 1.2 grams of liquid olefines boiling under 80°. In the run at atmospheric pressure, ethylene is the only gaseous olefine of consequence (about 1.6 grams identified), whereas an ethylene-propylene mixture (about 1.1 grams) results from the run at 15 mm.

Trimethyl ethylene vapors apparently give little or no separation of carbon or hydrogen between 668° and 790°, at least at atmospheric pressure.[98] At 938°, a yellow-brown vapor is formed which has the following composition; methane, 27.7 percent; ethylene, 8.1 percent; hydrogen, 1.76 percent; acetylene, 0.3 percent; carbon, 5.09 percent; benzene, 8-13 percent; tar, 34-39 percent. The quantity of methane is more than is required for the cleavage of one methyl group.

According to Ostromislensky,[99] at sufficiently high temperatures all open chain hydrocarbons with one double bond, as well as saturated cyclic hydrocarbons, undergo pyrolysis into a saturated hydrocarbon and butadiene. In no case was Ostromislensky able to observe the production of hydrogen, nor was hydrogen mentioned in the work of Norris and Reuter [100] except to state that "there appeared to be no free hydrogen produced". Parenthetically, it may be stated that although the latter statement may be true, the data in the article of Norris and Reuer do not give very satisfactory evidence of its absence since no recorded attempt was made to analyze for it. Ostromislensky's work would lend support for the equation:

$$CH_3—CH(CH_3)—CH=CH_2 \longrightarrow CH_4 + CH_2=CH—CH=CH_2,$$

to represent the cracking of *iso*propyl ethylene, but it is obvious from the above discussion that this reaction should be considered merely as one of the reactions of the pyrolysis. The same may be said concerning the formation of butadiene by the thermal decomposition of other hydrocarbons. A patent, relative to the production of isoprene from amylene, specifies [101] that the reaction proceeds by passing amylene through a tube heated to redness.

Finally, Engler's [102] experiments with trimethylethylene are of an altogether different type. By heating 350 grams for a month in a sealed glass tube at 320°, there is formed a complex mixture, chiefly of paraffins and naphthenes. The 10 liters of gas is composed of 91.1 percent (by volume) saturated hydrocarbons, 7.4 percent hydrogen and

[98] Haber, *Chem. Zentr.* **1896** (2) 570; Haber and Oechelhauser, *ibid.* **1897** (1) 225.
[99] Ostromislensky, *J. Russ. Phys. Chem. Soc.* **47**, 1974 (1915).
[100] Norris and Reuter, *J. Am. Chem. Soc.* **49**, 2626, 2628 (1927).
[101] Perkin, Weizmann, Matthews, Strange, Brit. Pat. 5,932, 1910; U. S. Pat., 991,453, 1911; Perkin, *J. Soc. Chem. Ind.* 619 (1912).
[102] Engler and Routala, *Ber.* **42**, 4620 (1909).

1.5 percent unsaturated hydrocarbons. In the liquid are *n*- and *iso*-pentane, hexane, heptane, octane, nonane and the naphthenes (C_nH_{2n}) from hepta- to pentadeca- inclusive.[103] A small amount of cyclohexane may also be identified.

Methyl propyl ethylene behaves quite analogously when heated under pressure. The gaseous products are saturated for the most part and the liquid contains a mixture from hexane to dodecanaphthene. One-third of the liquid is unsaturated.

Ipatiew noted the similarity of results with ethylene (p. 60) and amylene, and suggested that part of the results with amylene are due to a preliminary decomposition into ethylene.

No other olefine seems to have been studied except hexadecene. This investigation, similar to that of hexadecane (pp. 73-75) was carried out by Gault and Altchidjian.

Hexadecene.

This olefine was prepared in 25 percent yields (pure) by the distillation of cetyl palmitate [104] at 300-400 mm.:

$$C_{15}H_{31}—CO—O—C_{16}H_{33} \longrightarrow C_{15}H_{31}—CO_2H + C_{14}H_{29}—CH=CH_2.$$

Decomposition of hexadecene [105] appears to commence between the two singly linked carbon atoms at the end of the molecule. Between the low temperatures which condition the formation of mono- and di-ethylenic chain hydrocarbons, and the high temperatures at which aromatic hydrocarbons and tar are formed, there is an intermediate zone within which the decomposition products include a series of more or less saturated hydrocarbons; these, by loss of hydrogen, may be converted into the substances formed at high temperatures. At 50 cc. per hour, through tubes 64 cm. and 16 cm. long, gas formation begins at 450° and 580° respectively. In the gas, the maximum percentage of unsaturated hydrocarbons (67-8 percent) and the minimum percentage of saturated hydrocarbons (25-7 percent) occurs at 575° and 700° respectively for the two tubes. In the long tube, hexadecene disappears at 650°, and naphthalene is isolable.

Dienes.

Allene. Preliminary experiments with allene,[106] in which the gas was conducted through an empty pyrex tube (hot portion, 2 ft.), indi-

[103] Compare Routala, *Petroleum* **5**, 321; *Chem. Abstracts* **4**, 2369 (1910).
[104] Krafft, *Ber.* **16**, 3022 (1883).
[105] Gault and Altchidjian, *Compt. rend.* **178**, 1562, 2092 (1924); *Ann. chim.* [10] **2**, 209-268 (1924); *Mat. grasses* **16**, 7006 (1924); **17**, 7039, 7071 (1925).
[106] Hurd and Spence, unpublished data.

cate that the main product is a liquid polymer if the temperature is either 460° or 520°. None of this is obtained, however, at temperatures of 600° or above. At 460° (rate of flow of 92 cc. per minute), no carbon is deposited in the tube; at 520-550°, some carbon; at 600° or higher, so much carbon is deposited that it clogs the tube. The production of hydrogen and methane is coincident with the formation of carbon, since very little is formed at the low temperatures, but large amounts appear at the high temperature. Acetylenes may be produced (by rearrangement) even at the low temperature; certainly, allene is not the exclusive unsaturated hydrocarbon in the effluent gases.

Butadiene-1,3 and Isoprene. On p. 60, the details relative to the large formation of aromatic hydrocarbons from butadiene at 800° have been mentioned. Similarly, when isoprene is passed through a glass tube at 750° at 19 cc. per hour, the isoprene gives 56.1 percent of tar,[107] half of which is benzene; toluene, etc., 28 percent; and naphthalene, 11 percent. One quarter which boils at 230-400° consists of methyl naphthalene, anthracene, phenanthrene and chrysene, whereas the other quarter is pitch and carbon. Of the gases, which comprise 33.7 percent by weight of the reaction product, one seventh is ethylene contaminated with some butadiene, three fifths is methane, and one quarter hydrogen. In a high vacuum at 750-800°, isoprene remains largely unaltered.

The polymerization of isoprene to rubber by heating in an autoclave will be discussed in a later chapter. The time varies from 10 hours to several days, and the temperature from 90-250°.

Hexadiyne, $CH_3—C{\equiv}C—C{\equiv}C—CH_3$, is rather stable to heat, unless subjected suddenly to red heat,[108] when it gives a carbonaceous residue. Guest has found [109] that heptyne-1, $C_5H_{11}—C{\equiv}CH$, rearranges somewhat on passing it through a pumice-filled tube at 350°. The effluent condensate is a mixture of heptyne-1 (68 percent) and other isomers.

[107] Staudinger, Endle and Herold, *Ber.* **46**, 2467 (1913).
[108] Griner, *Ann. chim. phys.* [6] **26**, 357 (1892).
[109] Guest, *J. Am. Chem. Soc.*, **50**, 1746 (1928).

Chapter 4.

Cyclic Hydrocarbons.

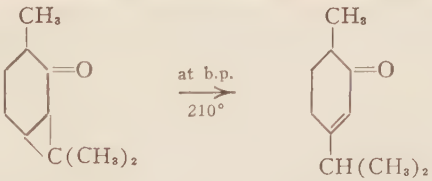
Aliphatic Hydrocarbons.

At a temperature of 550° or higher *cyclopropane* [1] is converted into its isomer, propylene. Trautz and Winkler [2] have shown that at 600° this is a reaction of the first order. Mention may be made of the remarkable catalytic effect [3] of platinum black, which causes rearrangement of 40-45 percent of the cyclopropane at 100°.

According to the German patent 252,499 by the Badische Co. and Schmidt,[4] a mixture of butadiene and ethylene is obtained by heating tetrahydrobenzene (obtained from cyclohexyl bromide) in a quartz tube at 500°. Thus the reaction:

$$C_6H_{10} \longrightarrow C_4H_6 + C_2H_4.$$

Certain terpene derivatives, such as carone, umbellone and thujone, which are bicyclic, change into monocyclic compounds by heating. These compounds are cyclic ketones, but the essential change for our consideration is a change from a cyclopropane ring to a double bond.



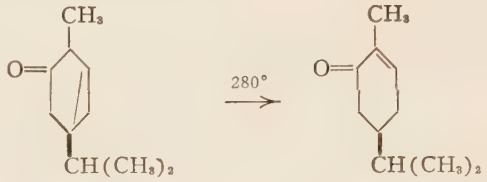
carone [6] *carvenone*

Thymol is formed quantitatively by heating for 18 hours in a sealed tube at 280°.

umbellone [6] *thymol*

[1] Berthelot, *Compt. rend.* **129**, 490 (1899).
[2] Trautz and Winkler, *J. prakt. Chem.* **104**, 53 (1922).
[3] Tanatar, *Z. physik. Chem.* **41**, 735 (1902).
[4] Schotz, "Synthetic Rubber," New York, D. Van Nostrand Co., **1926**, p. 43.
[5] Baeyer, *Ber.* **27**, 1920 (1894).
[6] Semmler, *Ber.* **40**, 3993 (1908).

Thujone yields 20 percent carvotenacetone, after purification through the oxime.



thujone[7] *carvotenacetone*

Cyclopentane and cycloheptane, and also *n*-hexane, are unchanged when heated at 200-300° with a palladium catalyst,[8] but under these conditions, *cyclohexane* gives much hydrogen. Under rather varied conditions, Ipatiew [9] reported a reverse order of stability. From his results, cyclohexane appears to be more stable than *n*-hexane, as illustrated by the following comparative runs.

TABLE XIV. *Comparison of Pyrolysis of n-Hexane and Cyclohexane.*

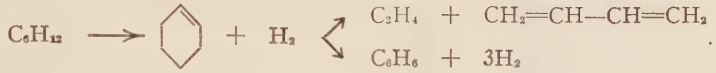
	Original Weight Grams	Temperature °C.	Time Hours	Gas Liters	Liquid Grams	Boiling Point of Liquid °C.
Hexane	90	710	2	17	67	37-72
Hexane + Alumina	100	660	2.5	34	46	36-74
Cyclohexane ...	65	750	1	12	35	38-84
Cyclohexane + Alumina	65	740	1	13	39	42-87

The gas from hexane without the catalyst was composed of 50 percent C_nH_{2n}, 8.4 percent H_2, 41.6 percent C_nH_{2n+2}, and approximately the same composition was found with the catalyst. From cyclohexane, the analysis was 44.5 percent, 14 percent and 42 percent respectively for olefines, hydrogen and saturated hydrocarbons.

When heated for 4 hours with alumina at 110 atmospheres, cyclohexane isomerizes somewhat into methylcyclopentane (also giving olefines, benzenes, polymethylenes, etc.), but with ordinary pressure, even at 760°, there is no such isomerization. In fact, there is no such conversion [10] in 3 days in sealed tubes at 350°, whereas at 420° the yield of methylcyclopentane in 3 days is no more than 5 percent. In other cyclohexane derivatives, all changes seem to occur in the substituents rather than in the ring. Thus, phenyl cyclohexanecarboxylate rearranges into cyclohexyl *o*-hydroxyphenyl ketone; and cyclohexyl phenyl ether into *o*-cyclohexyl phenol, together with some cyclohexene and phenol.

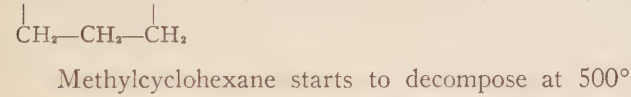
[7] Semmler, *Ber.* **27**, 895 (1894); **33**, 2454 (1900).
[8] Zelinski, *Ber.* **44**, 3121 (1911).
[9] Ipatiew, *Ber.* **37**, 2961 (1904). Ipatiew and Dowgelewitsch, *Ber.* **44**, 2987 (1911).
[10] Skraup and Beifuss, *Ber.* **60**, 1070 (1927).

D. T. Jones [11] reported that when cyclohexane is heated to 500° in contact with porous porcelain, as much as 40 percent of hydrogen is formed together with about 26.1 percent of benzene and higher olefines, 21.9 percent of ethane and any excess of cyclohexane, 3 percent of methane, and 8.5 percent of ethylene. The presence of only 0.2 percent of acetylene makes it very unlikely that it is the precursor of benzene. Jones suggested the following reactions as the most probable:



A patent [12] has been issued concerning the decomposition of cyclohexane and related compounds, by passing the vapors over a hot spiral of platinum, or carbon, or quartz or aluminum silicate, whereby some butadiene is formed.

Ostromislensky [13] mentions the production of butadiene-1,3 by passing the vapors of ethylcyclohexane over the hot coils of Andreev's "isoprene lamp":



Methylcyclohexane starts to decompose at 500°, and at 530° the gaseous products analyze as follows; hydrogen, 42.1 percent; methane, 22.5 percent; ethylene, 10.6 percent; ethane, etc., 12 percent; benzene and higher olefines, 12.8 percent. The large increase in methane over that from cyclohexane is reasonable because of the methyl group. Acetylene does not appear.

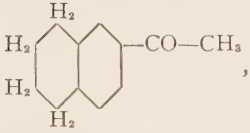
Dihydrobenzoic acid gives benzoic acid by heat.[14] 1,4-Dihydronaphthalene (Jones) initially decomposes at 390°. At 430°, it is transformed into much naphthalene and a gas which, by volume, is 85.4 percent hydrogen and 14.6 percent methane. Tetralin is more stable, but it pyrolyzes at 490°. At 530°, there is much naphthalene and gas, the latter analyzing as follows; 80.2 percent hydrogen, 9 percent methane, 4 percent ethane, 3 percent ethylene, 3.3 percent benzene and higher olefines. The chief products in both cases are hydrogen and naphthalene in conformity with the principle of least molecular deformation.

From these results it is evident that there is a fundamental difference in the stability of the C-H linking in open chain paraffins and

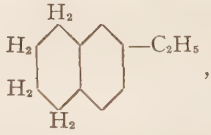
[11] Jones, *J. Chem. Soc.* **107**, 1582 (1915).
[12] F. Bayer and Co., Brit. Pat. 448, 1912.
[13] Ostromislensky, *J. Russ. Phys. Chem. Soc.* **47**, 1974 (1915).
[14] Eichengrun and Einhorn, *Ber.* **23**, 2887 (1890).

in cyclohexane or in the hydrogenated naphthalenes. So also, the latter deviate decidedly from the true aromatic structures in their reactions of pyrolysis.

Results on substituted tetrahydronaphthalene derivatives are of unusual interest, inasmuch as substitution processes in the aromatic half of tetralin and in tetralin obey different rules. Were a suitable means of dehydrogenation to be found, then a synthesis of hitherto inaccessible derivatives of naphthalene would be effected. In some cases, it has been found that pyrogenic methods are quite satisfactory for this dehydrogenation. Thus, the best way to prepare methyl-β-naphthyl ketone,[15] free from the α-ketone, is to pass methyl-β-tetralyl ketone,

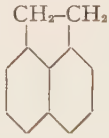


, through a tinned-iron tube at 680-700°. In 30 minutes, 10 grams of the latter pyrolyzes to produce a 3 gram yield of the pure naphthyl ketone. Some naphthalene is formed as well. At 600-620° there is little change, and at 750° some dinaphthyl appears because of a secondary reaction. β-Ethyl tetralin,

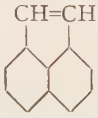


, behaves similarly. At 600°, very little happens; at 650°, in a carbon dioxide atmosphere, from 50 grams in 1.5 hours a yield of 10 grams of pure β-ethyl naphthalene results. Fifty degrees higher than this, much naphthalene contaminates the product. Another pyrolytic method of converting tetralin derivatives into those of naphthalene will be described later (see p. 141).

Acenaphthene,



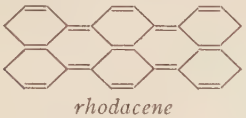
, loses two hydrogen atoms when it is distilled in a carbon dioxide atmosphere through a quartz tube. Although acenaphthylene,



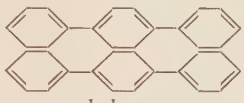
, is formed, at least three other hydrocarbons are also isolable, namely, leucacene, rhodacene and chalcacene.[16] Probable structures for these compounds are given below.

[15] von Braun, Hahn and Seemann, *Ber.* **55**, 1687 (1922).
[16] Dziewonski, *Ber.* **45**, 2493 (1912); **53**, 2173 (1920).

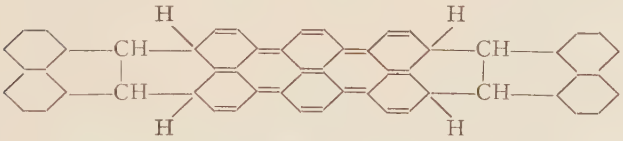
Rhodacene is intensely colored, dark violet, and passes into the more stable, copper-red chalcacene. Leucacene is thought to be made up from two acenaphthylene residues and one of rhodacene; it is colorless but the surface reddens in the air. By direct heating, or by heating in nitrobenzene, leucacene changes into rhodacene.



rhodacene

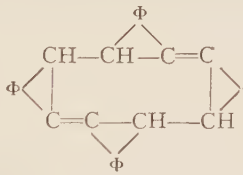


chalcacene



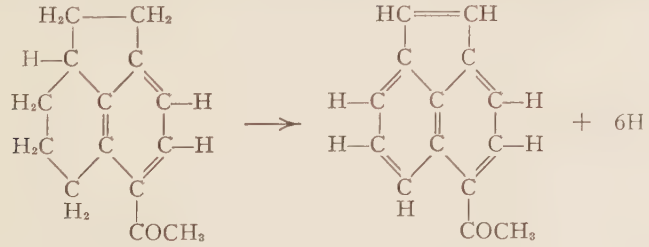
leucacene

In this connection, it may be stated that acenaphthylene [17] polymerizes at as low a temperature as 90°. The best yields of polymer, $(C_{12}H_8)_n$, where n is probably 22, come at 200° by short heating or by longer heating at 110°. This polymer changes into a red liquid at 345-350°, and then boils energetically, giving off acenaphthene, acenaphthylene and a residue which contains fluorocyclene and decacyclene. It is suggested that fluorocyclene is



, wherein $\Phi =$ $C_{10}H_6$. If acenaphthylene is maintained for 30 minutes at 290°, the products are "polyacenaphthylene", 70-73 percent; acenaphthene, 3-4 percent; fluorocyclene, 4-5 percent; and decacyclene, 2 percent.

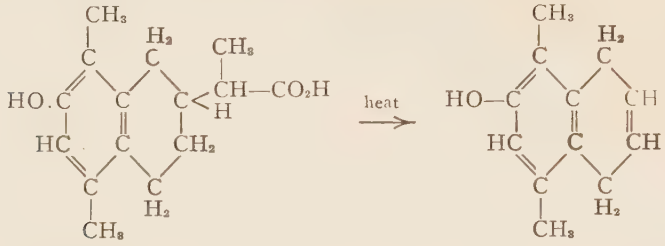
The following conversion [18] at 700° gives 20 percent yields. About 70 percent of a mixture of unchanged material and acenaphthylene accompanies it. This will be mentioned again in the chapter on ketones.



Acetyl-tetraphthene *Acetyl-acenaphthylene*

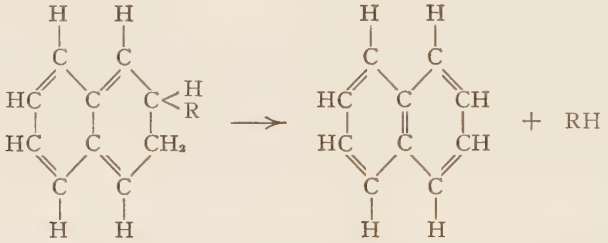
[17] Dziewonski and Leyko, *Ber.* **47**, 1679 (1914).

Anthracene and hydrogen are rapidly formed when the vapors of 9,10-dihydroanthracene [18] are passed through a glowing tube. The following case [19] is curious in that hydrogen is not evolved:

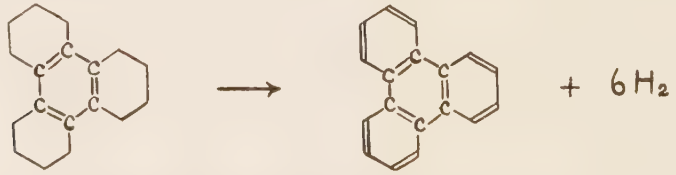


Santonous Acid

Jones and Wheeler [20] employ a similar type of reaction to explain the formation of naphthalene derivatives from hydrogenated nuclei in coal. Thus:



An interesting synthesis of triphenylene from cyclohexanone is described by Mannich.[21] Cyclohexanone is condensed to dodekahydrotriphenylene by a synthesis of the "acetone to mesitylene" type, and this is then distilled over copper at 450-500° in a carbon dioxide atmosphere. The quantity of hydrogen which is evolved approaches the theoretical amount.

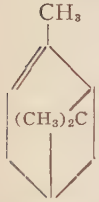


Phenyl-cyclohexylidene-cyclohexyl-methane, $\begin{matrix} C_6H_5 \\ C_6H_{11} \end{matrix}\!>\!C\!=\!C\!<\!\begin{matrix} CH_2\text{—}CH_2 \\ CH_2\text{—}CH_2 \end{matrix}\!>\!CH_2$ is stable [22] in the air at 330°.

[18] Lucas, *Ber.* **21**, 2511 (1888); *also*, Meyer and Hofmann, Monatsh. **37**, 681 (1916).
[19] Cannizzaro, *Gazz. chim. ital.* **13**, 385 (1884).
[20] Jones and Wheeler, *J. Chem. Soc.* **105**, 2563 (1914).
[21] Mannich, *Ber.* **40**, 159 (1907).
[22] Conant, Small and Sloan, *J. Am. Chem. Soc.* **48**, 1746 (1926); Gray and Marvel, *ibid.* **47**, 2796 (1925).

The dehydrogenation of $\Delta_{2,5}$-dihydroterephthalic dimethyl ester only yields one-seventh to one-sixth of the theoretical amount of hydrogen [23] after several hours of heating at 230° in a boiling thymol bath. This is at variance with Baeyer's statement [24] that dimethyl terephthalate could be formed in good yields at 100°. Baeyer's results may have been due to oxidation by the air; Knoevenagel's experiment was conducted in a carbon dioxide atmosphere.

A complex mixture of hydrocarbons is formed by pyrolyzing pinene,



, in a red hot iron tube.[25] Among the hydrocarbons formed are benzene, xylene, toluene, naphthalene, anthracene, phenanthrene and methyl anthracene.

Aromatic Hydrocarbons.

Benzene.

It has long been known that benzene differs quite materially from the aliphatic hydrocarbons in its behavior towards heat. In the first place, it is more stable than its paraffin analog, *n*-hexane. Haber determined this fact by comparative runs with these two compounds. Secondly, instead of a scission of the C—C bond which is so common in aliphatic hydrocarbons, benzene undergoes pyrolysis in such a way as to promote C—H scission. Thus, hydrogen and diphenyl are the chief products:

$$2C_6H_6 \longrightarrow C_6H_5—C_6H_5 + H_2.$$

This result has received the interpretation of Haber's rule, and also the rule of least molecular deformation. Furthermore, it has recently been pointed out [26] that coke formation comes from benzenoid hydrocarbons and not from paraffin hydrocarbons since the latter can be cracked at moderate temperatures without forming coke. As Brooks states, this is "another way of saying that heat causes splitting of the carbon-to-carbon bond in the paraffin hydrocarbons but in the aromatic series, in which the remarkably stable six-carbon ring structure is present, the result is chemical condensation, carbon-to-carbon combination to larger and larger molecules and eventually to coke, with the

[23] Knoevenagel and Bergdolt, *Ber.* **36**, 2857 (1903).
[24] Baeyer, *Ann.* **251**, 292 (1889).
[25] Berthelot, *Ann. chim. phys.* [3] **39**, 5 (1853); [4] **16**, 165 (1869).
[26] Brooks, *Ind. Eng. Chem.* **18**, 521 (1926).

liberation of hydrogen and other simple split-products such as methane, ethylene, etc."

Berthelot [27] found that if benzene is introduced into a glowing porcelain tube, 35 cm. long, at a rate of 1 gram per minute, the chief product is diphenyl, although carbon, hydrogen sulfide, acetylene and chrysene were also noted. Schultz [28] checked Berthelot's results, and reported a 25-30 percent yield of diphenyl (based on the unrecovered benzene) if either a porcelain or iron tube was used, but practically no yield if a glass filling was employed. In one run, Schultz obtained a 37 percent yield (98.5 grams of diphenyl from 728 — 462 grams of benzene in 3.5 hours). Schmidt and Schultz [29] improved this to 60 percent, by adding benzene at a rate of one drop in three seconds through a glowing iron tube. After the recovery of unused benzene from 2 kg. originally, there were obtained 700 grams of diphenyl, 40 grams of *p*-diphenylbenzene, an equal quantity of *m*-diphenylbenzene, and an undetermined quantity of triphenylene. In confirmation of this, Bachmann and Clarke [30] have recently reported that no *o*-diphenylbenzene was detectable from the residues of 5 kg. of pyrogenic biphenyl, but fairly large amounts of *m*- and *p*-diphenylbenzene and a small amount of triphenylene were isolable. *o*-Diphenylbenzene apparently is not the responsible factor in the formation of triphenylene, since it gives only biphenyl and a little carbon on passage through a hot tube and some of it is unchanged. The presence of triphenylene from benzene was also confirmed by Mannich,[31] who obtained 2 grams of pure material from 800 grams of solid reaction products (the crude yield would have been much more).

With the use [32] of a sloping iron tube, 36 cm. long, heated for 20 minutes at 720°, a 70 percent yield of diphenyl may be attained. Prior to its entry into the tube, benzene is vaporized by dropping it into an attached copper flask at 150°. Similar experiments were performed between 600-800° and with 7-42 minutes' heating. Apparently, dilution of the benzene vapors to 23 percent benzene by volume with steam [33] enables one to use higher temperatures without the formation of by-products. The conditions in the patent stipulate 700°, a pressure of 60 lbs. per sq. in., and a contact surface such as pumice. Below 500°, benzene is scarcely affected. The optimum temperature [34] for diphenyl

[27] Berthelot, *Ann. chim. phys.* [4] **9**, 453 (1866); **12**, 52, 185 (1867); **16**, 143, 172 (1869); *Compt. rend.* **62**, 965 (1865); **63**, 479 (1866).
[28] Schultz, *Ann.* **174**, 204 (1874).
[29] Schmidt and Schultz, *Ann.* **203**, 118 (1880); Olgiati, *Ber.* **27**, 3385 (1894).
[30] Bachmann and Clarke, *J. Am. Chem. Soc.* **49**, 2091 (1927).
[31] Mannich, *Ber.* **40**, 164 (1907).
[32] Smith and Lewcock, *J. Chem. Soc.* **101**, 1453 (1912).
[33] Weiss and Downs, U. S., 1,322,983; *Chem. Abstracts* **14**, 287 (1920).
[34] Zanetti and Egloff, *Ind. Eng. Chem.* **9**, 356 (1917).

formation is 750°, although at this temperature diphenyl-benzene is also noted. Below 800°, there is no evidence of ethylene or of naphthalene in the reaction products, but carbon is formed. According to Meyer and Hofmann,[35] the lowest temperature for diphenyl formation is 650°, and at this temperature diphenyl-benzene also appears. Other investigators [36] have noticed diphenyl as low as 550°, but certainly its yield under these conditions must be inappreciable. At 750°, diphenyl-benzene accompanied the formation of diphenyl, but no naphthalene or unsaturated compounds could be found. These latter experiments were performed in an atmosphere of nitrogen. With a hydrogen atmosphere instead of nitrogen, the production of diphenyl is practically checked. A mixture of 92 percent hydrogen and 8 percent benzene gives only traces of diphenyl in an otherwise comparable run. In fact, the reverse reaction, diphenyl to benzene, appears to be established under these conditions.

Diphenyl may also be formed [37] by passing benzene vapors over an electrically heated carbon, platinum or nickel filament. The details for such a method have been worked out satisfactorily [38] by Lowe and James. With a nichrome filament at yellow-red heat, 1 kg. of diphenyl may be formed in a 24 hour run, using 110 volts and 10-12 amperes. In the electric arc, benzene, in common with other hydrocarbons [39] both aliphatic and aromatic, is pyrolyzed into a gaseous mixture of acetylene, methane, ethane and hydrogen (see p. 52). By using an electric arc (25-30 amperes and 30-35 volts) in benzene, Müller and Bänninger [40] obtain evidence for the preliminary dissociation of benzene into the C_6H_5— and the H—C≡C— radicals, and the various ways that these radicals combine provide the explanation for the isolated products. These products include the following;

(1) Benzene (about 95 percent); phenyl acetylene, diphenyl and anthracene. The phenyl acetylene has never before been noted in other investigations of this type.
(2) Butadiyne, H—C≡C—C≡C—H, which was isolated by rapid cooling to prevent polymerization. Some higher acetylenes are also formed.
(3) Gases, of which 86-88 percent are hydrogen, and 9-10 percent are acetylene.

The equation of benzene to diphenyl and hydrogen calls for hydrogen as the only gaseous product of the reaction. Analysis reveals 92-94 percent hydrogen and 5-3 percent methane, when the experiment of pyrolysis is performed [41] in an 11 cm. platinum tube at 1150°. The

[35] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[36] Cobb and Dufton, *Chem. Trade J.* **63**, 197 (1918); *Gas World* **69**, 127 (1918).
[37] Loeb, *Z. elektrochem.* **8**, 777 (1902).
[38] Lowe and James, *J. Am. Chem. Soc.* **45**, 2666 (1923).
[39] Contardi, *Atti congresso naz. chim. ind.* **1924**, 358; *Chem. Abstracts* **19**, 1941 (1925).
[40] Müller and Bänninger, *Helv. Chim. Acta* **10**, 763 (1927).
[41] Peytral, *Bull. soc. chim.* **29**, 44 (1921).

methane was considered by Mlle. Peytral to come from the diphenyl and not from the benzene. Pyl [42] considers that an essential intermediate substance from benzene to diphenyl is dihydrodiphenyl. This is based on the observation that the equation

$$2C_6H_6 \longrightarrow C_{12}H_{12},$$

shows a decrease in gaseous volume, a reaction which should be facilitated by pressure. Actually, diphenyl is formed in a bomb tube at 300°, whereas not a trace of it comes from benzene at 300° and atmospheric pressure. According to Fuchs, however, Pyl's experiments appear insufficient to establish the mechanism of the formation of diphenyl since, in the control experiment, only the small quantity of benzene present in vapor form in the part of the apparatus heated to 300° is subject to reaction, whereas in the sealed tube experiment, the entire quantity (10 cc.) reacts.

A perusal of some of the older work on this subject leads one to believe that the sequence *benzene to naphthalene to anthracene* is actually established. In view of the fact that no naphthalene or anthracene has been reported from experiments in which pure benzene vapors were used as the starting material, this position becomes untenable. The sequence instead, for temperatures below 1000°, is *benzene to diphenyl to diphenyl-benzene,* etc. The formation of naphthalene and anthracene is usually noticed, however, when a mixture of benzene and toluene, or a mixture of benzene and ethylene, or when other similar mixtures are subjected to thermal decomposition. The pyrolysis of toluene will be mentioned later. The yield of anthracene at 925°, based on the reaction:

$$2C_6H_6 + C_2H_4 \longrightarrow C_{14}H_{10} + 6H$$

is 0.675 percent (quartz tube). This reaction [43] is strongly endothermic, but only small yields of anthracene can be formed since it will not form at low temperatures (none at 800°), and since it decomposes above 900°. At 925°, the sum of the yields of diphenyl and of carbon is at a minimum, but at 1000°, there is only carbon formation. Ferko's work [44] was similar; he passed a mixture of benzene and ethylene through a hot iron pipe, and from 1240 grams of unrecovered benzene he obtained 300 grams of diphenyl, 17 grams of styrene, 15 grams of anthracene, and 10 grams of phenanthrene.

The type of condensation of benzene to diphenyl is not particularly apparent in the homologs of benzene. These will be discussed later.

[42] Pyl, *Ber.* **60**, 1133 (1927); Fuchs, *Ber.* **60**, 1663 (1927).
[43] Zanetti and Kandall, *Ind. Eng. Chem.* **13**, 208 (1921).
[44] Ferko, *Ber.* **20**, 660 (1887).

However, such compounds as naphthalene, thiophene, or such derivatives of benzene as diphenyl-methane, or diphenyl ether do condense in this manner. Naphthalene gives dinaphthyl, but diphenyl-methane yields fluorene, showing this to be an intermolecular condensation. Reactions of the latter type are fairly common when five- or six-membered rings may be formed. The following cases illustrate this behavior.

Naphthalene.

Naphthalene, by pyrogenic decomposition,[45] yields hydrogen and a mixture of α,α- and β,β-dinaphthyl, $C_{10}H_7—C_{10}H_7$. Possibly the α,β-isomer is also formed. Neither naphthalene nor anthracene decomposes [46] to form monocyclic compounds. A yield of 130 grams of dinaphthyl [47] may be formed in 8 hours from 380 grams of naphthalene (thus, 850 grams minus 470 grams recovered). Much carbon is in the tube also.

Pyridine.

Pyridine [48] is transformed into dipyridyl by passing it through a red hot glass tube.

Thiophene.

Thiophene [49] is stable at 340°, but at red heat in a platinum tube it gives hydrogen and small amounts of the isomeric dithienyls.

Diphenyl Oxide.

This changes into diphenylene oxide [50] in good yields at sufficiently elevated temperatures. Most of the hydrogen of the reaction is consumed in reducing diphenyl oxide to phenol and benzene.

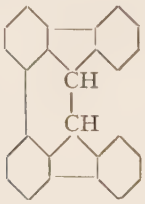
Diphenyl-methane.

Diphenyl-methane,[51] similarly, yields fluorene, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!>\!CH_2$, and here again, hydrogen is not liberated in any appreciable quantity, but it is consumed in the formation of benzene and toluene. Small amounts of anthracene and of diphenyl have also been noted [35] when a red heat is maintained for 7 hours.

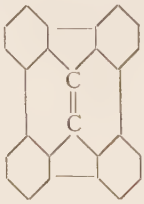
[45] Smith, *Ber.* **9**, 467 (1876); *Chem. News*, **22**, 296.
[46] Rittman, Byron and Egloff, *Ind. Eng. Chem.* 7, 1023 (1915).
[47] Ferko, *Ber.* **20**, 662 (1887). Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[48] Roth, *Ber.* **19**, 360 (1886).
[49] Nahnsen, *Ber.* **17**, 789 (1884); Auwers and Bredt, *Ber.* **27**, 1747 (1894).
[50] Graebe and Ullmann, *Ber.* **29**, 1877 (1896). Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[51] Graebe, *Ber.* **6**, 127 (1873); *Ann.* **174**, 195 (1874).

Fluorene.

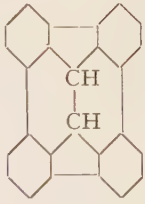
Fluorene itself is not entirely resistant to heat.[52] For the most part it escapes unchanged when passed at reduced pressure through a red hot quartz tube containing a coil of wire, but some difluorenylene, rubicene, and small amounts of dihydrorubicene are formed. This is the best way to make rubicene. Pummerer and Ulrich[53] state that rubicene is $C_{26}H_{14}$, but Dziewonski and Suszko defend their formula of $C_{26}H_{12}$.



Difluorenylene



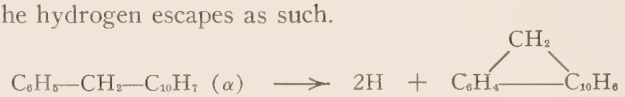
Rubicene



Dihydrorubicene

Phenyl α-Naphthyl Methane.[54]

This undergoes pyrolysis into chrysofluorene. Very probably, but little of the hydrogen escapes as such.



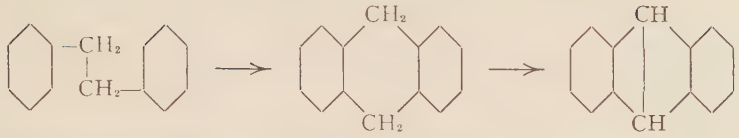
Stilbene and Symmetrical Diphenyl Ethane.

Conflicting reports exist in the literature relative to the behavior of stilbene and of symmetrical diphenyl ethane at high temperatures. Graebe[51] reported phenanthrene, much toluene, and no hydrogen from the former, and from the latter, stilbene and toluene. Stilbene may be isolated if the reaction is performed at reduced pressure:

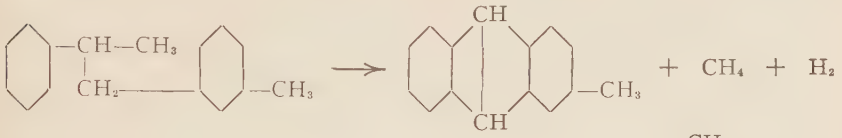
$$2C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2C_6H_5CH_3.$$

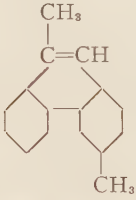
Phenanthrene is also stated to be a by-product. It is interesting to compare this with the results from ethane, wherein ethylene, methane and hydrogen are formed. In contrast to Graebe's results, Meyer and Hofmann[35] found no phenanthrene nor anthracene from stilbene. However, they agree that diphenyl ethane is pyrogenically decomposed to stilbene, and they also noted a small quantity of toluene. Anthracene appears to be a major product, and since this was not obtained with stilbene, a mechanism through dihydroanthracene is suggested. Actually, this compound is readily changed into anthracene at a red glow. Thus:

[52] Dziewonski and Suszko, *Chem. Abstracts* **17**, 1459 (1923).
[53] Pummerer and Ulrich, *Ber.* **58**, 1806 (1925). Dziewonski and Suszko, *Ber.* **58**, 2544 (1925).
[54] Graebe, *Ber.* **27**, 954 (1894); Scholl and Seer, *Ber.* **44**, 1672 (1911).



The mechanism proposed by Meyer and Hofmann is readily adaptable to the results which are reported by other investigators[55] with homologs of symmetrical diphenyl-ethane. Thus, β-phenyl-α-m-tolyl-propane (called m-xylene-styrene, since it is synthesized from m-xylene and styrene in the presence of sulfuric acid) decomposes very smoothly into methyl anthracene when its vapors are passed through a glowing (dark red) tube. The equation to represent this change is:



On the mechanism of Graebe, a dimethyl phenanthrene,  , (or possibly a monomethyl-phenanthrene), would have been anticipated. In exactly the same way, α-xylyl-β-phenylpropane (synthesized from styrene and unsymmetrical trimethylbenzene) changes into dimethyl anthracene. The smooth nature of the pyrolysis is evident from the yield of 15 grams from 20 grams of the original material:

$$C_6H_5CH(CH_3)—CH_2C_6H_3(CH_3)_2 \longrightarrow C_6H_4{<}\begin{matrix}CH\\|\\CH\end{matrix}{>}C_6H_2(CH_3)_2.$$

When α,β-diphenyl-propane (from styrene and toluene) is passed through the glowing tube, anthracene results, but because of the high reaction temperature which is necessary, only a fraction of it escapes as such. In a comparative run with pure anthracene through the same tube, only 9 percent of that which was introduced was recovered.

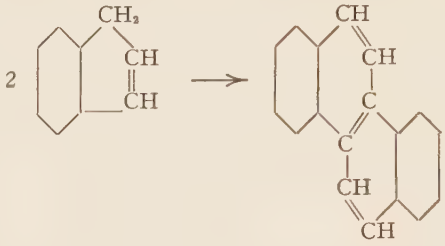
Other Aromatic Hydrocarbons.

Symmetrical di-α-naphthyl ethylene[56] appears to follow Graebe's mechanism, in that picene, $\begin{matrix}C_{10}H_6—CH\\|\quad\quad\|\\C_{10}H_6—CH\end{matrix}$, is the recorded product. Picene

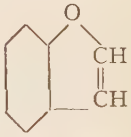
[55] Kraemer, Spilker and Eberhardt, *Ber.* **23**, 3272 (1890).
[56] Hirn, *Ber.* **32**, 3342 (1899).

is also liberated from petroleum residues by energetic distillation.[57] Furthermore, 1-phenyl-2-α-naphthyl-ethane yields chrysene,[58] whereas on Meyer and Hofmann's mechanism one would have expected naphthanthracene.

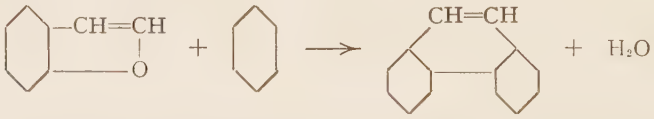
Another case wherein chrysene is formed as the result of a high temperature reaction is in the pyrolysis of indene. From 100 grams of indene, Spilker [59] recovered 75 grams and obtained 15 grams of chrysene, merely by passing it through a hot tube.



Chrysene is also produced when naphthalene and cumarone,

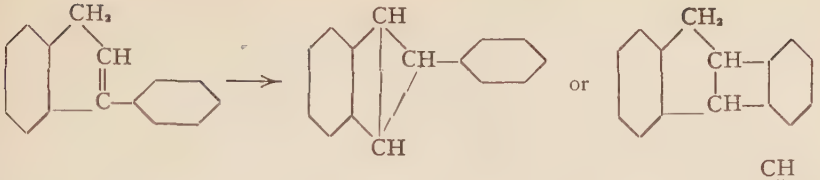


are passed through a hot tube (with a yield of 4.5 grams from 100 grams of the mixture). The production of phenanthrene [60] from benzene and cumarone is entirely analogous. In this case, the equation is

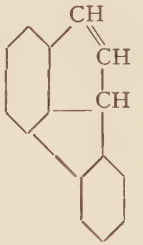


These reactions are of interest in the formation of phenanthrene and chrysene from coal tar, inasmuch as cumarone is also a product of the distillation of coal tar. It collects in the fraction which has a boiling point of 168-175°. Because of the formation of chrysene from indene, it might be expected that phenyl indene would lead to the production of diphenyl chrysene, but apparently this is not the case. When the vapors of α-phenyl indene [61] are heated in a pumice-filled porcelain tube to dull redness at 16 mm. in a carbon dioxide atmosphere, it undergoes isomerization in accordance with the following equation:

[57] Graebe and Walter, *Ber.* **14**, 174 (1881).
[58] Graebe and Bungener, *Ber.* **12**, 1078 (1879).
[59] Spilker, *Ber.* **26**, 1545 (1893).
[60] Kraemer and Spilker, *Ber.* **23**, 84 (1890).
[61] Mayer, Sieglitz with Ludwig, *Ber.* **54**, 1397 (1921).

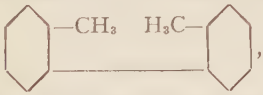


The compound which was expected, namely, fluoranthene,



was not formed. The substance which was produced was not reducible by sodium in alcohol, or by hydrogen and a palladium catalyst, nor could it be oxidized by potassium dichromate in acetic acid. With permanganate, the oxidation produced benzil-*o*-carboxylic acid. Although α-phenyl indene is changed by a pyrogenic distillation, this is not the case with α-methyl indene, or with α-phenyl-β-methyl-indene.

It may be noted in passing that indene changes [62] to a resinous mass if heated for 100 hours in a sealed tube at 180-260°, from which tribenzylene-benzene (truxene) may be liberated by subsequent higher heating with a free flame. A small yield of truxene results from heating 25 hours at 260° in a sealed tube, but the chief product is tetraindene, $(C_9H_8)_4$. The latter, by higher heating yields truxene [63] in 50 percent yields, and also indene and hydrindene. Cyclopentadiene, with a structure related to indene, gives [35] neither naphthalene nor other aromatic compounds when it is exposed to red heat.

If benzene can change so readily to diphenyl it would be surprising if diphenyl would not continue to undergo pyrolysis in this manner. It has been found [35] that *diphenyl* does decompose at elevated temperatures into 4,4′-diphenylbiphenyl. Similarly, *anthracene* changes into dianthryl. *o,o′*-Ditolyl, 

, utilizes the side-chains, and is converted into phenanthrene, with possibly small quantities of diphenanthryl also formed.

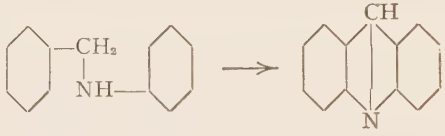
N-Heterocyclic compounds, such as carbazole, acridine, etc., may be synthesized in excellent yields from the corresponding phenylated de-

[62] Stobbe and Zschoch, *Ber.* 60, 473 (1927).
[63] Bruson, *Ber.* 60, 1094 (1927).

rivatives. Thus, carbazole[64] is prepared in good yields by heating diphenylamine:

$$(C_6H_5)_2NH \longrightarrow (C_6H_4)_2NH + 2H.$$

The hydrogen undoubtedly reduces a portion of the diphenylamine to benzene and aniline. Benzanilide pyrolyzes very smoothly into phenanthridone: $\begin{matrix} C_6H_4\text{—}CO \\ | \quad\quad | \\ C_6H_4\text{—}NH \end{matrix}$. The synthesis of acridine[65] from benzyl aniline gives such excellent yields that it is recommended as its best method of preparation.



Three benzal amines, the ones from aniline, naphthylamine and *o*-toluidine, all give different type reactions when they are heated. Benzal aniline[66] yields phenanthridine:

$$\begin{matrix} C_6H_5\text{—}CH \\ \quad\quad \| \\ C_6H_5\text{—}N \end{matrix} \longrightarrow \begin{matrix} C_6H_4\text{—}CH \\ | \quad\quad \| \\ C_6H_4\text{—}N \end{matrix} + H_2.$$

Phenanthridine is isomeric with acridine, and its properties are very closely related to it. However, in this reaction it seems rather well established that acridine is not formed. The yield of phenanthridine is small, and the major portion of the decomposition[67] leads to benzonitrile and benzene, together with ammonia and hydrogen cyanide from more deep-seated decompositions. When benzal aniline is passed through the hot tube in dilution with nitrogen at a (gaseous) rate of 120-150 cc. per minute, the yields of phenanthridine respectively for 700°, 750°, 800° and 900° are 1.6 percent, 1.9 percent, 2.3 percent and 0.7 percent. Below 700° the yield is negligible. At these temperatures, the yields of benzonitrile are 21.7 percent, 33.9 percent, 28.3 percent, and 12.4 percent. A porcelain tube was used in these experiments. Practically the same yields of phenanthridine result with an iron tube, but the porcelain tube does assist somewhat in bettering the yield of nitrile (39.9 percent at 800°).

Benzal α-naphthylamine, when passed over heated pumice,[68] is converted into a naphthacridine (originally thought to possess a chrysidine

[64] Graebe, *Ann.* **167**, 125 (1873); **174**, 180 (1874).
[65] Meyer and Hofmann, *Monatsh.* **37**, 698 (1916); *see also*, Pictet and Gonset, *Chem. Zentr.* **1897**, I, 414.
[66] Pictet and Ankersmit, *Ber.* **22**, 3340 (1889); *Ann.* **266**, 138 (1891).
[67] Pyl, *Ber.* **60**, 287 (1927).
[68] Pictet and Ehrlich, *Ann.* **266**, 155, 163 (1891). Ullmann and LaTorre, *Ber.* **37**, 2923 (1904).

structure, related to phenanthridine). Benzal β-naphthylamine behaves similarly. The equation to represent this is:

$$C_6H_5{-}CH \underset{N{-}C_{10}H_7}{\parallel} \longrightarrow C_6H_4{<}\begin{matrix}CH\\|\\N\end{matrix}{>}C_{10}H_6 + H_2.$$

Benzal *o*-toluidine,[69] $C_6H_4{<}\begin{matrix}CH_3\\N{=}CHC_6H_5\end{matrix}$, gives about a 30 percent yield of phenyl indole, $C_6H_4{<}\begin{matrix}CH{=}\\NH\end{matrix}{>}C{-}C_6H_5$, by conducting its vapors through a glowing tube. In this case the presence of the *o*-methyl group is the determining factor.

The Influence of Side Chains.

Toluene.

The study of the pyrolysis of toluene dates back to the time of Berthelot.[70] He found that toluene was pyrogenically decomposed into benzene, naphthalene, an oil of boiling point 280°, anthracene and chrysene. Graebe[71] checked these results and found in addition, phenanthrene. By passing mixed vapors of benzene and toluene through a red hot tube, Carnelley[72] identified benzene, naphthalene, diphenyl, phenyl-tolyl, ditolyl and higher compounds. The work of Ferko,[73] although it paid little attention to accurate temperatures and no attention to pressures, was very important in showing the yields of the reaction. His method was to pass the hydrocarbon vapors through an iron pipe, heated to redness for 40 cm. of its length. In terms of the original toluene, 13.8 percent was recovered, 11.5 percent converted into benzene, 2.1 percent into diphenyl, 0.5 percent into styrene, 3 percent into naphthalene, 1 percent into anthracene and 1.1 percent into phenanthrene. The presence of ethylene did not change the results materially.

Meyer and Hofmann[74] furnished a fundamental contribution by showing that the methyl group in toluene is largely retained by the aromatic nucleus at dull red heat. Under these conditions for 4-8 hours, dibenzyl but no benzene is formed. At higher temperatures (light red), much of the dibenzyl changes further into stilbene, and in addition, there is formed phenyl tolyl methane and ditolyl methane.

[69] Pictet, *Ber.* **19**, 1064 (1886).
[70] Berthelot, *Ann. Chim. Phys.* [4] **9**, 445 (1866); **12**, 5 (1867); **16**, 143 (1869).
[71] Graebe, *Ber.* **7**, 48 (1874).
[72] Carnelley, *J. Chem. Soc.* **37**, 701 (1880).
[73] Ferko, *Ber.* **20**, 660 (1887).
[74] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916); **38**, 343 (1917).

Ethyl Benzene.

According to Ferko's experiments ethyl benzene is broken down more easily than toluene, as only 4 percent was recovered. The yield of benzene in this case is 15 percent, toluene 1 percent, styrene 2 percent, diphenyl 0.6 percent, naphthalene 2.2 percent, anthracene 0.4 percent and phenanthrene 2.6 percent. Compared with toluene, the important differences seem to be a greater yield of styrene and of phenanthrene. Meyer and Hofmann identified stilbene from ethyl benzene. Their results, furthermore, show that the scission is between the two carbon atoms of the side chain, and in this respect resembles toluene, which also holds the α-carbon atom tenaciously. Symmetrical diphenyl ethane, a compound which is related to ethyl benzene, has already been discussed.

p-Xylene.

This gives almost pure *p*-dixylyl, melting point 81°, at a light red glow (Meyer and Hofmann), and some of the xylene may be recovered. At a yellow glow, *p,p'*-dimethyl-stilbene, $(CH_3C_6H_4—CH=)_2$, is formed. From either *p*-xylene or from *p*-dixylyl at a yellow heat, there is obtained some dimethyl anthracene, but no such anthracene derivative comes during the pyrolysis of mesitylene. The latter changes almost exclusively into dimesityl, melting point 78°.

Various patents [75] have suggested the use of ethyl benzene, or xylene, or *o*- and *p*-ethyl-toluene, or diethyl benzene or 1,3,5-dimethyl ethyl benzene in the pyrogenic synthesis of styrene. Styrene or its homologs are produced between 450-700°, in terms of the patents. Hydrogen is evolved in the above cases. With cymene, methane is a product of the reaction. This work was stimulated because styrene polymerizes to a plastic,[76] when heated at 180-200° for three hours, or for a shorter time if heated under pressure.

Other Aromatic Hydrocarbons.

In a systematic study, Rittman, Byron and Egloff [77] pyrolyzed various aromatic hydrocarbons, making temperature and pressure the controlled variables. Temperatures of 650, 725, 800° and pressures of a vacuum, 1, 12 and 18 atmospheres were used. The rate of flow was 6 cc. per minute. On the basis of their evidence, they reach the conclusion that the course of the cracking reaction in the aromatic series

[75] Ostromislensky and Shepard, U. S. Pat. 1,541,175, Jan. 9, 1925; Can. Pat. 261,325, June 1, 1926; Brit. Pat. 232,909, Apr. 24, 1924. *Chem. Abstracts* **20**. 210, 424, 3461 (1926).

[76] Ostromislensky, Brit. Pat. 233,649, May 7, 1924; 236,891, July 12, 1924; *Chem. Abstracts* **20**, 1243 (1926).

[77] Rittman, Byron and Egloff, *Ind. Eng. Chem.* **7**, 1019 (1915).

may be indicated as follows, and that any reverse action is negligible: higher benzene homologs → lower benzene homologs → benzene → diphenyl → naphthalene → anthracene → carbon and gas. Such a statement as this needs interpretation, since it has been shown that pure benzene or pure diphenyl or pure anthracene behaves differently. It is not questioned that higher benzene homologs tend to yield benzene in large measure, but the very fact that these homologs have produced the benzene is sufficient indication that gaseous olefines such as ethylene or butadiene are present, and that these are the responsible factors in the synthesis of naphthalene or anthracene. Diphenyl is formed from benzene, but it plays little or no part in the production of naphthalene or of anthracene (see p. 96).

The percentage of original substance recovered after the heating of benzene, toluene, xylene or cymene decreases in the above order, and this may be taken as an index to the relative stability of the four compounds. The percentage yield of liquid reaction products decreases with an increase of temperature or pressure. The optimum conditions for benzene formation are 650-725° and a pressure of 1 to 12 atmospheres. This order of stability was also verified by Fischer,[78] who employed high temperatures and a hydrogen atmosphere. With sufficiently high temperatures, hydrogen causes a complete separation of the side-chain. Similarly, methyl naphthalene is readily split to methane and naphthalene. The synthesis of benzene by the high temperature reaction of mixed xylenes and hydrogen has also been studied [79] by Bradley and Parr. At temperatures up to 600° in an iron tube, the xylene is practically undecomposed. Various catalysts were used to bring the yield of benzene to 94 percent of the theoretical. Cobb and Dufton [80] have also noted that when a mixture of toluene and hydrogen is passed over hot coke, the chief reaction products are benzene and methane. In a nitrogen atmosphere, they noticed decomposition of toluene at 550°, and at 600° stilbene was isolable. Decomposition to naphthalene, anthracene and unsaturated compounds was extensive at 750°. Kling [81] has suggested that hydrogenation under pressure at high temperatures, namely, at the temperatures of thermal decompositions of organic compounds, should be a useful tool in the study of pyrolyses. He considers it probable that molecular hydrogen reacts with the nascent organic molecules at the instant when the original molecule dissociates, and if suitable conditions are chosen, only saturated hydrocarbons and no tars

[78] Fischer, Schrader and Meyer, *Ges. Abhandl. Kenntn. Kohle* **4**, 373 (1919); *Chem. Abstracts* **17**, 2272 (1923).
[79] Bradley and Parr, *Chem. & Met. Eng.* **27**, 737 (1922).
[80] Cobb and Dufton, *Chem. Trade J.*, **63**, 197 (1918); *Gas World* **69**, 127 (1918).
[81] Kling and Florentin, *Compt. rend.* **182**, 389 (1926).

should result. The method also allows molecules of differing stabilities to be distinguished.

Although naphthalene[82] itself gives no benzene on pyrolysis, methyl naphthalene does so. Calculated on the original oil, a 3.2 percent yield of benzene by volume is formed at 650° and 14 atmospheres; the yield of toluene is 2 percent, at 650° and 14 atmospheres, or 650° and 11 atmospheres. Above this temperature there is much carbon. The side chain in the original compound must, of course, be taken as the reason for this behavior, but the precise mechanism of the reaction is still obscure.

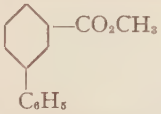
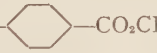
In an attempt to evolve a working hypothesis concerning the mechanism of the cracking process, S. Skraup[83] has studied the effect of heat on several *p*-anisyl alkanes, $CH_3O—C_6H_4—R$, wherein the attached alkyl groups (R) are normal propyl, butyl, pentyl, hexyl, heptyl and nonyl. At 300-320°, in tubes filled with nitrogen, the aryl paraffins with an even number of carbon atoms in the side chain (butyl, hexyl) undergo decomposition into the next lower homolog (propyl, pentyl). The terminal methyl group is detached, presumably as CH_2, which polymerizes to C_2H_4. Apparently, the side-chain residue does not rearrange. Contrasted with this, no decomposition is encountered up to 320° when the side-chain contains an odd number of carbon atoms, but at slightly higher temperatures anisole is gradually produced. The side-chain becomes completely detached, presumably as an olefine. The details of these sealed tube experiments are given below.

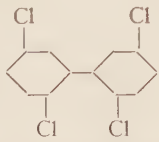
TABLE XV. *Effect of Heat on p-Anisyl Alkanes with Varying Alkyl Groups.*

Radical	Hours	Temperature	Percent Unchanged	Percent of Gas Produced
		When R is even.		
Butyl	17	310–320°	28	52.5 (*p*-propyl anisole)
	64	280–310°	22	30.8
	64	315°	42	43.7
Hexyl	18	280–310°	40	41.6 (*p*-pentyl anisole)
	24	290–315°	34	43.2 " "
	64	315°	42.5	37 " "
		When R is odd		
Propyl	19	310–320°	94	No gas produced
	64	280–310°	94	No gas produced
Pentyl	64	290–315°	93.7	
	24	310–320°	62.5	10 (anisole)
	64	315°	92	No gas; no anisole
Heptyl	18	280–310°	65	No gas
	19	310–320°	60	19 (anisole); much gas + phenolic by-products
Nonyl	64	315°	86	No gas produced

[82] Egloff, *J. Soc. Chem. Ind.* **35**, 920 (1916).
[83] Skraup and Nieten, *Ber.* **57**, 1294 (1924).

The discussion of the pyrolyses of aromatic compounds which possess reactive groups will be deferred in most cases, since the interesting effect is occasioned by the group in question rather than by the aromatic nucleus. It is interesting, however, to record the following cases.

Benzoic acid not only undergoes pyrolysis [74] to benzene and benzaldehyde, but also gives the nuclear condensation products of diphenyl and the acids, $C_6H_5—C_6H_4—CO_2H$ and $HO_2C—C_6H_4—C_6H_4—CO_2H$. Obviously, such effects only occur at very high temperatures, so far as organic compounds are concerned. *Methyl benzoate* is fairly stable at dull red heat, but at this temperature, ethyl benzoate is rapidly transformed into benzoic acid and ethylene. With more vigorous heating, methyl benzoate gives benzene, diphenyl, trioxymethylene, and the esters  and  . The unusual stability of the $—CO_2CH_3$ group is apparent from the results with methyl *p*-toluate, which yields methyl stilbene-4,4′-dicarboxylate, $CH_3O_2C—C_6H_4—CH=CH—C_6H_4—CO_2CH_3$ and trioxymethylene at high temperatures. This is comparable to the behavior of toluene.

Aromatic halogen compounds, in which the halogen is attached to the nucleus are known to be very inert. This behavior is also apparent in pyrolytic reactions. There is no evidence, except possibly with some of the iodides, that the two aromatic nuclei become joined by the carbon atoms which hold the halogens. Thus, *p-dichlorobenzene* is very stable, and only after continued maintenance [84] at high temperature is it changed into tetrachlorodiphenyl,  . Similarly, phenyl chloride becomes transformed into 4,4′-dichlorodiphenyl, together with some of the 2,2′-isomer; hydrogen chloride is formed and some *p*-chlorodiphenyl, $Cl—C_6H_4—C_6H_5$, also. Phenyl fluoride changes into 4,4′-difluorodiphenyl and it is noteworthy that it undergoes pyrolysis with considerably more difficulty than does its homolog, *p*-fluorotoluene. The latter is converted quickly, and at lower temperatures, into the stilbene derivative, $F—C_6H_4CH=CHC_6H_4F$. Phenyl iodide undergoes decomposition into benzene, diphenyl and a mixture of iododiphenyls. *p*-Iodotoluene yields not only 4,4′-diiodo-stilbene, but also stilbene itself, and

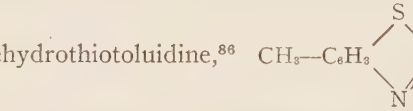
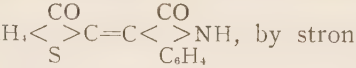
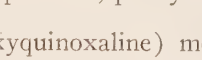
[84] Meyer and Hofmann, *Monatsh.* **38**, 141 (1917).

also toluene and symmetrical diphenyl ethane. Other cases of this nature will be presented in the chapter on halogen compounds.

It is interesting to record a few aromatic compounds which melt or boil at fairly high temperatures without undergoing appreciable decomposition.

TABLE XVI. *Compounds Which Boil without Decomposition.*

Compound	Boiling Point
m-Diphenyl benzene	363°
1,1,2-Triphenylpropane	365°
Triphenyl carbinol	Above 360°
9-Phenyl anthracene	417°
Anthrapurpurin	462°
Benzidine	400°
Triphenylmethane	359°
Anthraquinone	382°
Alizarin	430°
Flavopurpurin	459°

In addition to these quinquephenyl has a melting point of 388.5° (*Ber.*, **57**, 2886 (1924)); indanthrene[85] tolerates heating in the air to 470°; dehydrothiotoluidine,[86]  , has a boiling point of 434°; thionaphthene-2-indol-(3′)-indigo,[87]  , by strong heating gives orange-yellow vapors, almost without decomposition; phenylene oxamide,  , (or its enol, 2,3-dihydroxyquinoxaline) melts at 410°; and oxamide, in a sealed tube, melts at 417°.

[85] Scholl and Berblinger, *Ber.* **36**, 3429 (1903).
[86] Green, *Ber.* **22**, 970 (1889).
[87] Bezdrik and Friedlaender, *Monatsh.* **29**, 375 (1908).

CHAPTER 5.

PETROLEUM, RUBBER AND RELATED HYDROCARBONS.

Petroleum.

Undoubtedly, the petroleum industry with its cracking processes ranks as the greatest organic chemical industry. From this, one would assume that much is known about it. This is true insofar as the art of it is concerned, but the chemistry of the process is still largely undeveloped. No systematic survey [1] of the cracking art will be presented, but a brief attempt will be made to correlate the chemistry of this process with the known facts from pure hydrocarbons. Since the scope of this book is limited to compounds, rather than mixtures, no extended account will be attempted.

The cracking of petroleum was noticed [2] by Silliman in 1855, and again "accidentally discovered" in 1861 by a workman in a Newark, N. J., refinery. The fact that liquid hydrocarbons may be obtained in quantity when paraffin (melting point 46°) is heated under pressure was established [3] over half a century ago by Thorpe and Young. From 3.5 kg. of the paraffin, these investigators isolated 0.3 liter which boiled below 100°, 1 liter of boiling point 100-200°, and 2.7 liters of boiling point 200-300°. The products were shown to be paraffin or olefine hydrocarbons, C_5 and above. Scarcely any gases were formed. Since gases (under C_5) are readily formed by decomposition of the hydrocarbon vapors at higher temperatures, e.g. 700°, it may be inferred that the position of cleavage varies with the temperature. The following experiment [4] resembles that of Thorpe and Young. From 300 cc. of paraffin (melting point 50° and specific gravity 0.925), there results 305 cc. of a liquid (specific gravity 0.770) if the paraffin is heated in a 1100 cc. vessel till the pressure attains 800 pounds. When cool, the pressure of the residual gas becomes reduced to 130 pounds. Sixteen percent of the

[1] For good articles on the subject, *see* Engler and Höfer, "Das Erdöl," 1909. Bacon and Hamor, "American Petroleum Industry," New York, McGraw-Hill, 1916, vol. II; Lomax, Dunstan and Thole, *Ind. Eng. Chem.* **9**, 879-902 (1917); Padgett, *Mechanical Engineering* **42**, 400 (1920); *Chem. Met. Eng.* **23**, 908 (1920); Burton, *Ind. Eng. Chem.* **14**, 159 (1922); Dean and Jacobs, Technologic Paper 258, Bureau of Mines (1922); Johnson, *Mechanical Engineering* **46**, 879 (1924); Dunstan and Pitkethly, *J. Inst. Petr. Tech.* **10**, 728-774 (1924); Gault, *Bull. soc. ind. Mulhouse* **91**, 439 (1925); Burrell, *Ind. Eng. Chem.* **20**, 605 (1928).

[2] Peckham, *Am. J. Sci.* [2] **47**, 9 (1869); Silliman, *Am. Chemist* **2**, 18 (1871); Leet, *Petroleum Distillation*, New York, 1884.

[3] Thorpe and Young, *Proc. Roy. Soc.* (London) **19**, 370 (1871); **20**, 488 (1872); **21**, 184 (1873). *Chem. News* **23**, 124 (1870); *Ber.* **5**, 556 (1872); *Ann.* **165**, 1 (1873).

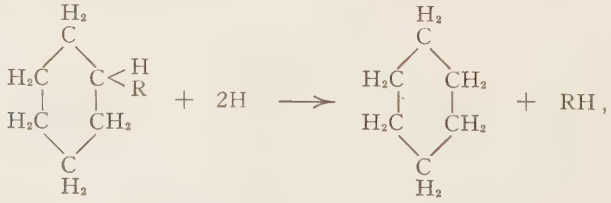
[4] Snelling, *Bull. Am. Inst. Mining Eng.* **1915**, 695. *Chem. Abstracts* **9**, 1841.

liquid, or 48 cc., distils below 150°. By repetitions of the process, it was found that 70 percent of the paraffin is convertible into gasoline, the remainder being largely gas plus some carbon. Herbst [5] has cracked solid paraffin (melting point 50-52°) by boiling it for 42 hours at 300-400° in the presence of activated charcoal. Four kg. of the paraffin was found to yield 2.835 kg. of distillate.

Except in its complexity, the cracking of petroleum should not differ fundamentally from the pyrolysis of hydrocarbons which have already been taken up. A study of individual hydrocarbons, therefore, gives a basis for tracing the fate of the primary products of cracking. The added complexity is due to the nondescript nature of petroleum. It is to be expected that the reactions are not merely those of pyrolysis, but also include simultaneous reactions of pyrosynthesis, due to the interaction of two or more components (either present originally or subsequently) of the mixture. This should be especially true, since the reactions of cracking usually are of considerable duration.

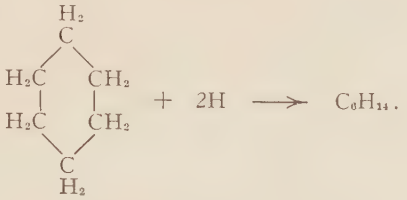
The principle of electron attraction (p. 28) which postulates scission of a hydrocarbon into radicals of low electron attraction during pyrolysis, leads to an interesting conclusion regarding the products of cracking; namely, that the cracked hydrocarbons should tend to become straight chain compounds. In other words, the nature of the cracked distillates can be no true index of the structure (normal or branched-chain) of the original paraffin in the oil. This conclusion is based on the consideration that tertiary alkyl groups should exert less electron attraction than secondary or primary; hence, the position of cracking should take place at the branched carbons if any are present, thereby deleting the tertiary atoms.

Ipatiew [6] has suggested a reaction mechanism which is stimulating. In brief, he postulates the pyrolysis of paraffin into smaller olefines, the latter undergoing rearrangement into a cycloparaffin (thus, a homolog of α-hexylene into a homolog of cyclohexane). Given a supply of hydrogen, which may be one of the reaction products, he postulates scission of side chains of the cyclic body by reduction:



[5] Herbst, *Z. angew. Chem.* **39**, 194 (1926).
[6] Ipatiew and others, *Ber.* **44**, 2978, 2987 (1911); **46**, 1748 (1913).

and further, reduction of this cyclohexane into hexane:



Although most of the gasoline from cracking processes is made by liquid-phase processes, vapor-phase cracking is receiving a strong impetus at the present time because of the superior anti-knock properties of the gasoline thus produced.[6a] Another advantage is that vapor-phase processes may operate at lower pressures, thereby enabling less expensive equipment. One of the drawbacks of vapor-phase cracking is the greater formation of fixed gases, but it may be pointed out that this gas is formed at the expense of the fuel oil rather than the gasoline.[6b] Roughly one thousand cubic feet of gas (27% ethylene, 16% propylene, 1% butadiene) is formed by vapor-phase cracking of one barrel of oil. The motor fuel which is thus produced appears to be high in unsaturated and in cyclic hydrocarbons, and to have very little paraffin hydrocarbon content. From our discussion with pure hydrocarbons, this would be expected since the unsaturated hydrocarbons appear to be more stable towards heat than the saturated. In passing, McKee has recently pointed out[6c] that several so-called liquid-phase processes actually operate at a temperature which must exceed the critical temperature of the oil. Therefore, they are actually vapor-phase processes in spite of the high pressures used.

The following quotation from Dean and Jacob's paper (*loc. cit.* Ref. 1, p. 7) gives a concise summary of the features of pressure distillation processes and the so-called vapor-phase processes. "Cracking by distillation without pressure is old, and has been in use for years for the production of kerosene from heavier petroleum products. It was early discovered, by accident, it is said, that vigorously fired stills, constructed with plenty of surface for reflux condensation, were capable of cracking heavy hydrocarbons into distillates which were largely of the volatility range required for kerosene or lamp oil. The pressure-distillation process was developed when gasoline, instead of kerosene, became the product most needed. The difficulties involved in the development and operation of the pressure-distillation process were considerably

[6a] Little, *Chem. Met. Eng.* **35**, 14 (1928); Morrell, *ibid.*, p. 560; Owen, *ibid.*, pp. 610, 677.
[6b] Wagner, *Chem. Bulletin* (Chicago), **15**, 371 (1928).
[6c] McKee and Parker, *Ind. Eng. Chem.* **20**, 1169 (1928).

greater than those that must have been encountered in the cracking distillation of kerosene.—

"The mechanism of the pressure-distillation type of process is indicated by the title. A charge of oil is distilled under a pressure that permits the maintenance of temperatures high enough to cause cracking. The gasoline formed is removed continuously by distillation, and the heating continues until the maximum amount of cracking that has been found economically desirable is attained. Success and safety in the operation of such a process are, of course, dependent to a great degree upon the details of equipment and procedure, and the applicability of the process is limited to types of oil that do not introduce excessive mechanical difficulties. Oils of too low a boiling point, that is, of too high vapor pressure, such as kerosene distillate, necessitate the carrying of pressures that are considered too high for safety, and they can be cracked only when present in relatively small proportion with other less volatile distillates. Oils with too great a content of asphaltic or pitchy constituents are considered unsuitable on account of their tendency to deposit excessive quantities of carbon.

"The pressure-distillation process is one that seems decidedly advantageous as to chemical kinetics. The temperatures maintained in the body of liquid oil are relatively low. In fact, the Burton patents specify a temperature ranging from 340° to 450° C. The temperature of the metal surfaces that transmit heat to the oil is undoubtedly considerably higher, but the results of the process warrant considering it as operating at a relatively low temperature. The desired product, gasoline, is removed from the cracking zone practically as soon as it is formed. The gasoline is volatile under the temperature and pressure conditions maintained in the still and passes promptly into the vapor line. These conditions of low temperature and prompt removal of gasoline favor a high yield of volatile liquid hydrocarbons with a minimum formation of those undesirable products—carbon and permanent gas.

"The disadvantages of pressure-distillation processes chiefly concern operating conditions. The stills commonly used have a high fuel consumption, which may or may not be necessary. The most important disadvantage concerns the safety of the workers. The care with which pressure-distillation processes have been and are operated has kept down the number of accidents to a very moderate figure, but it is a fact, nevertheless, that there is a considerable danger when a large body of oil is heated to a temperature sufficient to cause cracking. Pressure-distillation processes are subject to the further limitation of working to the best advantage only with a type of oil that is free from asphaltic

material and has a relatively high boiling point. In stating these disadvantages the authors do not wish to give the impression that in their opinion any other type of process is necessarily preferable to the pressure-distillation type; it is simply their purpose to indicate that, in spite of its advantages from a chemical point of view, there is need for other processes handling a wider range of raw material and not requiring such extreme care in operation.

"The other common type of thermal process is that in which oil is cracked by passage through some sort of system, generally a tubular one, that is strongly heated. Whether the oil is completely vaporized previous to cracking during its passage through the heated zone is questionable, but as regards chemical behavior this type of process has characteristics indicating a single-phase or vapor-phase system. In the distillation type of process there is for each oil a relation between temperature and pressure. With the vapor-phase type the two conditions of temperature and pressure can be fixed independently of each other and of the physical properties of the oil cracked, which according to the phase rule makes it possible to regard the cracking zone as a single-phase of vapor-phase system.

"The vapor-phase processes have been developed along commercial lines, with a number of modifications, but they seem to differ chiefly in mechanical and operating details, the fundamental mechanism seemingly being the same. A stream of oil is passed through the heated zone of the cracking system, the latter being maintained at a temperature high enough to bring about the desired degree of conversion. Vapor-phase cracking processes practically always operate under pressure, although, as has been stated, this is not an absolute essential as it is for pressure-distillation processes. The temperatures usually measured are those of the cracked products leaving the heated zone, and the figures generally specified in patent claims or in descriptions of processes are between 500° C. and 600° C.

"As regards chemical action in vapor-phase processes it appears that the gasoline formed by cracking is not removed continuously but remains with the uncracked oil during its entire course through the cracking furnace. This results in the exposure of the gasoline to cracking conditions for an appreciable interval of time after its formation and gives an opportunity for recracking and consequent formation of permanent gas. On this account, as well as on account of the fact that the temperatures are undoubtedly higher than those effective in the pressure-distillation type of process, the amount of gas formed per unit

quantity of gasoline produced is higher in vapor-phase than in the pressure-distillation processes.

"Most of the vapor-phase processes with which the authors are familiar are believed to be more economical in fuel consumption than the pressure-distillation processes. As only a relatively small quantity of oil is in the system at any time, the danger is less if the equipment fails. Vapor-phase processes seem no more successful than pressure-distillation processes in handling oils containing asphaltic material, but have been found to crack satisfactorily the more volatile products, such as kerosene distillate, which pressure-distillation processes usually handle only in limited degree".

Burton's process of pressure-distillation, the first cracking process to be commercially successful,[7] submits the high boiling distillates (above 225°) from the crudes to temperatures of 370-400° under about 5 atmospheres pressure. This pressure is sufficient to prevent the original oil from distilling, but permits the "cracked hydrocarbons" to distil away. Although it was advocated for a time that condensation of the cracked distillates under pressure would lead to saturated hydrocarbons, such does not seem to be the case.[8] The distillation in Burton's process proceeds [9] at an average rate of 1-2 percent per hour for a 48 hour run. A 35 percent yield of gasoline, boiling to 232° C., is obtainable.

Many other processes have been successfully developed since Burton's, most of them averaging 25-35 percent of gasoline based on the original oil. Coke formation has been perhaps the greatest stumbling-block in the development of the art of cracking. In most cases, this has necessitated the use of selected cracking stocks, but processes have recently been developed which are not limited in this manner. This is particularly true of the Dubbs process,[10] which is "processing oils of less than one percent to over 25 percent by weight of the oil going to coke under the heat and pressure conditions of the system while producing yields of gasoline from 15 to over 78 percent by volume of the oil being processed". A comparison of natural and of cracked gasoline distillates shows that both contain paraffins, naphthenes, aromatics, olefines (small amount in natural), and a small quantity usually of compounds of nitrogen and sulfur. The cracked gasoline contains more aromatics and more olefines. In addition, it contains diolefines.[11]

[7] Burton, Perkin Medal Address, *Ind. Eng. Chem.* **14**, 159 (1922). Wilson, *ibid.*, **20**, 1099 (1928).

[8] Waterman and Reus, *Rec trav. chim.* **43**, 87 (1924).

[9] Padgett, *see* reference 1.

[10] Egloff, "Simultaneous Topping, Cracking and Coking of Heavy Oils by the Dubbs Process," *Petr. Devel. and Techn. in 1925*, **1926**, 346-358.

[11] Concerning diolefines, *see* Brooks, *Ind. Eng. Chem.* **18**, 522 (1926).

Petroleum chemists regard the nature, both physical and chemical, of an oil to be of secondary importance as compared with the influence of temperature, time and pressure. This is no doubt true, because of the fact that oil is such a complex mixture, and because of the secondary reactions which must come into play because of prolonged heating. This, however, is no basis for the assumption that one pure hydrocarbon pyrolyzes in exactly the same manner as another, and indeed it has been shown in the previous chapters that this is far from what actually occurs.

The production of aromatic hydrocarbons from petroleum requires higher temperatures than are usually used in cracking for gasoline production, and this is precisely what would be expected from the results with pure hydrocarbons. Rittman's is the best known modern process for aromatics. Temperatures of 600-1000° C. and pressures of at least 6 atmospheres are used. The oil is cracked in the gaseous phase, and the retorts are kept free of carbon. Usually the cracking is done in the presence of such fixed gases as hydrogen, methane, ethylene or ethane, whose formation by cracking is not desired. From some types of American petroleum, the optimum temperature for the production of benzene [12] is 750° (yield, 4.7 percent); of toluene, 650° (yield, 3.1 percent); and of xylene, 700° (yield, 1.9 percent). At 800° 2 percent naphthalene and 0.3 percent anthracene are produced.

The production of much larger amounts of benzene and toluene in the cracking of solvent naphtha [13] at 500-800° and 11 atmospheres pressure in steel tubes is not an analogous case. Solvent naphtha, instead of being aliphatic for the most part, contains large amounts of such cyclic compounds as indene and cumarone. About 16 percent of benzene, based on the total naphtha, and 20.6 percent of toluene were formed at 800° and 750° respectively. In terms of the liquid distillate, this represents 42.5 percent and 39.9 percent respectively.

Aromatic hydrocarbons may thus be formed either from polycyclic (asphaltic) hydrocarbons which are originally present; or they may be produced by dehydrogenation of naphthenes, which are known to be present; or, finally, they may be synthesized from unsaturated aliphatic hydrocarbons, particularly from the dienes or from the acetylenes. The mechanism for the production of aromatic hydrocarbons from such unsaturated hydrocarbons has been mentioned earlier (pp. 61 and 86).

The production of gas from petroleum occurs at temperatures between 750-1000°. An analysis of such a gas [14] showed 44.8 percent

[12] Egloff and Twomey, *J. Phys. Chem.* **20**, 121 (1916).
[13] Egloff and Moore, *Ind. Eng. Chem.* **9**, 40 (1917); **10**, 8 (1918).
[14] Noyes, Blinks and Mory, *J. Am. Chem. Soc.* **16**, 688 (1894).

methane, 20.5 percent hydrogen, 16.2 percent ethylene, 11.9 percent propylene and traces of other products. This result is of interest at this time in emphasizing the fact that temperature is one of the important controlling factors governing the extent of pyrolysis. Gasoline production is usually performed at much lower temperatures.

Turpentines and Other Terpenes.

From turpentine, isoprene may be formed in about 1-5 percent yields, if its vapors are passed through an empty glass tube at 600°, a porcelain-filled glass tube at 500°, or an empty iron pipe at 450°. These are optimum temperatures.[15] Toluene and higher homologs of benzene also appear, a maximum yield of toluene (10 percent) being noted at 500°. The yield of gases evolved increases steadily with an increase in temperature.

The decomposition of turpentine by heat was first investigated by Berthelot.[16] He was followed by Hlasiwetz,[17] Schultz [18] and Tilden.[19] Hlasiwetz passed turpentine vapors through a red-hot iron tube filled with porcelain, and obtained a liquid which had the odor of benzene, and from which, by fractionation, gave about 6 percent of a liquid boiling at about 30°. Tilden showed that this fraction was isoprene, and that it was identical to the isoprene obtained by Williams [20] from the distillation of rubber. Schultz obtained a liquid which contained the usual aromatic hydrocarbons from benzene to anthracene. Tilden showed that the difference in the work of Hlasiwetz and Schultz was merely due to a difference in temperature. The work of Schultz has recently been criticized by Fischer and Schrader.[21]

Other terpenes have also been shown to yield isoprene as a pyrolytic product. Harries and Gottlob [22] obtained 1 percent of isoprene from commercial pinene by means of an electrically heated platinum filament. Herty and Graham,[23] with a similar apparatus, obtained 5.5 percent (by volume) of isoprene from turpentine, and 8 percent from the pinene fraction which has a boiling point of 155-156°. From commercial limonene, Harries obtained 30-50 percent of isoprene, whereas Herty and Graham reported 12 percent from a limonene fraction. Staudinger and Klever [24] obtained a 60 percent yield of pure isoprene from limonene

[15] Mahood, *Ind. Eng. Chem.* **12**, 1152 (1920).
[16] Berthelot, *Ann. chim. phys.* [3] **39**, 5 (1853).
[17] Hlasiwetz, *Ber.* **9**, 1991 (1876).
[18] Schultz, *Ber.* **10**, 113 (1877).
[19] Tilden, *J. Chem. Soc.* **45**, 410 (1884); *Chem. News* **46**, 120 (1882).
[20] Williams, *Trans. Roy. Soc.* (London) **1860**, 241.
[21] Fischer and Schrader, *Brennstoff Chem.* **1**, 22 (1920); *Chem. Abstracts* **15**, 590 (1921).
[22] Harries and Gottlob, *Ann.* **383**, 228 (1911).
[23] Herty and Graham, *Ind. Eng. Chem.* **6**, 803 (1914).
[24] Staudinger and Klever, *Ber.* **44**, 2212 (1911). D. R. P. 257,640; U. S. Pat. 1,065,182, 1913.

by working in a vacuum of 2-3 mm. Here also, an electrically heated filament was used. Silberrad also had noticed [25] that a vacuum augments the yield of isoprene from turpentine.

Staudinger and Prodrom [26] obtain a 60 percent yield of isoprene from limonene in the following manner. Limonene vapors, at 20-30 mm. pressure, are warmed to 100° and passed downward (or upward, in other experiments) through a pyrogenic unit. This consists of a vertical brass tube (35 × 1.6 cm.), surrounded by a water jacket and maintained at 80-90°; inside this tube, but not touching it, is a coil (wound on a quartz support) of a meter-length of platinum wire of 0.5 mm. diameter. The wires are connected to a source of electricity and maintained at a suitable high temperature. The unchanged limonene is condensed by a freezing mixture and returned to the system, whereas the isoprene escapes and is condensed at — 80°. In this apparatus, myrcene (dimethyl-2,6-octatriene-1,5,7) gives about a 39 percent yield of crude isoprene.

Andreev [27] has also devised a kind of metallic (brass) isoprene lamp for the purpose of preparing isoprene from turpentine by exposure to a glowing platinum wire and also to a hot nickel wire coil. He reported that the addition of carvene or dipentene or aromatic hydrocarbons increased the yields of isoprene.

Schorger and Sayre [28] describe experiments in which turpentine or β-pinene vapors were passed through a hot iron tube filled with pumice, but found that much better yields of isoprene (8-9.6 percent) were obtained when they used a heated platinum wire filament. Evidence was obtained that this decomposition is partly thermal and partly catalytic, since a heated nichrome filament soon causes the deposition of enough carbon to short-circuit the wires. The patents on isoprene production in this manner are rather numerous, but they contribute little (see Mahood, Ref. 15) of general interest.

Semmler has studied [29] the decomposition of β-gurjunene under the influence of heat and pressure. It gives a brown liquid after being maintained for 12 hours in a bomb tube at 330°; fractionation of this liquid gives chiefly α-terpenes. The transformation of myrcene into camphorene (thus, $C_{10}H_{16}$ into $C_{20}H_{32}$) may be effected by several hours heating [30] in an iron tube at 250-260°. Squalene, or spinacene, is a substance with the empirical formula $C_{30}H_{50}$, which may be a mix-

[25] Silberrad, Brit. 4001, 1910, U. S. 1,022,338, 1912.
[26] Prodrom, Thesis, Zurich, 1913; Schotz, "Synthetic Rubber," New York, D. Van Nostrand Co., 1926. pp. 17, 93, 94.
[27] Andreev, *Chem. Zentr.* **1914**, II, 325; Schotz, *ibid.*, p. 47.
[28] Schorger and Sayre, *Ind. Eng. Chem.* 7, 924 (1915).
[29] Semmler and Jakubowicz, *Ber.* **47**, 1141, 2252 (1914).
[30] Semmler and Jonas, *Ber.* **46**, 1566 (1913).

ture of isomers. On dry distillation,[31] it gives trimethyl-ethylene as an initial pyrolytic product, later to be followed by a mixture of monoterpenes and dihydroterpenes. The third fraction, boiling point 120-170° at 20 mm., consists of a complex mixture of monocyclic sesquiterpenes, from which bisabolene has been isolated.

Smith has studied[32] the *rate of racemization of d-pinene* both in solution and in the gas phase at temperatures between 184° and 237°. The process is shown to be a simple unimolecular one. The rate is only 50 percent larger in the pure liquid than in the dilute gas, and is independent of surface and pressure. In this connection, it may be noted that racemization is not unusual in thermal processes. At 160°, active mandelic acid racemizes.[33] In contrast to this, however, Walden has recently shown[34] that ricinoleic acid, $CH_3(CH_2)_5$—CHOH—CH_2—CH=CH—$(CH_2)_7CO_2H$, shows an increase in its *d*-rotation at 200-300°. Either *α*- or *β*-stilbene chloride, C_6H_5—CHCl—CHCl—C_6H_5, partially reverts[35] to the other form at 200°. A transformation of a somewhat different type is the change of rhombic benzophenone-*α*, melting point 48°, into the monoclinic *β*-form, which melts at 26°. This change[36] may be brought about in 80 percent amounts by heating at 220°.

Rubber.

Since isoprene can be polymerized to rubber (see Chapter 26), it is natural to expect that isoprene is one of the products formed in the destructive distillation of caoutchouc. Historically, the latter fact was observed first. Rubber is completely decomposed at 300-350°.

In 1847, Himly[37] obtained two liquids by the pyrogenic distillation of caoutchouc. The lower boiling liquid, boiling point 33-34°, now called isoprene, Himly named "faradayin", in recognition of Faraday's service in determining[38] the composition of caoutchouc as $C_{10}H_{16}$. The higher boiling liquid, "caoutchine", boiling point 168-171°, is now called dipentene. Greville Williams, in 1860, also obtained[39] these substances by distilling rubber at as low a temperature as possible, but in addition, after purification, he established the structure of isoprene. Fifteen years

[31] Heilbron, Kamm and Owens, *J. Chem. Soc.* **1926**, 1630.
[32] Smith, *J. Am. Chem. Soc.* **49**, 43 (1927).
[33] Lewkowitsch, *Ber.* **16**, 2721 (1883).
[34] Walden, *Chem. Umschau Fette Oele Wachse Harze* **32**, 275 (1925); *Chem. Abstracts* **20**, 2660 (1926).
[35] Zincke, *Ann.* **198**, 134 (1879).
[36] Schaum and Rosenberger, *Z. anorg. allgem. Chem.* **136**, 329 (1924).
[37] Himly, *Ann.* **62**, 233 (1847).
[38] Faraday, *Quart. J. Sci.* **21**, 19 (1826).
[39] Williams, *Proc. Roy. Soc.* (London) **10**, 516 (1860); *Phil. Trans.* **150**, 254 (1860); Dinsmore, *Ind. Eng. Chem.* **18**, 1140 (1926) reviews this work, and others.

later, Bouchardat determined [40] the relative quantities of decomposition products. He subjected 5 kg. of fresh Para-rubber to distillation, and reported the formation of the following; about 40 liters of gas, chiefly carbon monoxide with some methane, and 10 grams of gas absorbed by bromine (ethylene and isoprene, etc.); isoprene, 250 grams; "caoutchine", probably dipentene, 2 kg. (boiling point 176-180°); a hydrocarbon, $C_{15}H_{24}$, 600 grams (boiling point 255-265°).

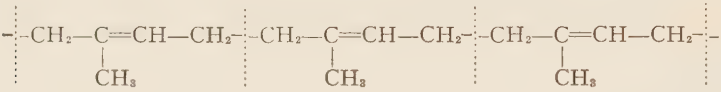
Both Williams and Bouchardat recognized the structural relationship of caoutchouc to its products of pyrolysis. Bouchardat stated: "In a word, one can say that caoutchouc is a certain hydrocarbon $(C_5H_8)_n$ which is decomposed by heat into a particular series consisting of polymerides of a single hydrocarbon C_5H_8, all the other distillation products, which parenthetically are present in small quantity, being due partly to impurities and partly to the breaking down of the products of distillation of caoutchouc". It was not until 1884 that Tilden established the fact that the low-boiling liquid obtained by the pyrolysis of rubber and of turpentine was one and the same substance, isoprene. In this year also, Wallach [41] established the identity of caoutchine and dipentene.

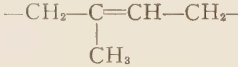
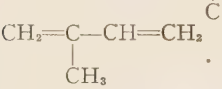
Aschan states [42] that 2-3 percent of isoprene is formed by distilling rubber. Quite recently, Staudinger and Fritschi [43] have performed distillation experiments on rubber which had been previously extracted with acetone and chloroform. They employed a high vacuum (0.1 mm.) and obtained 63.5 percent of distillate and 36.5 percent of resinous material. The distillate showed the presence of isoprene (3.1 percent of the total rubber), dipentene (8.8 percent), and about 8 percent of two unidentified hydrocarbons, $C_{15}H_{24}$ and $C_{20}H_{32}$.

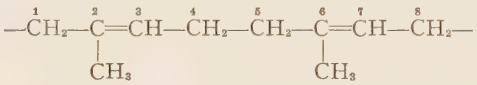
Without attempting to give a detailed account of the development of the structure of the rubber hydrocarbon, Staudinger's formula,[44] a huge continuous-chain molecule of indefinite size, appears to be most in accord with present data. Very probably, the chain of carbon atoms is twisted, so that certain carbon atoms represented as being far distant from others are actually close to them. Three units of Staudinger's formula follow:

[40] Bouchardat, *Bull. soc. chim.* **24**, 108 (1875).
[41] Wallach, *Ann.* **225**, 311 (1884).
[42] Aschan, *Öfvers Finska Vet. Soc.* **58**, 122 (1915); *Chem. Abstracts* **14**, 3655 (1920).
[43] Staudinger and Fritschi, *Helv. Chim. Acta* **5**, 785 (1922).
[44] Staudinger, *Ber.* **53**, 1081 (1920); in this reference, one of the methyls is inverted; correct formula in *Ber.* **59**, 3041 (1926).

From a consideration of the principles of electron attraction which have been developed (Chapter 2), it has been shown that the allyl group and related groups with the structure $>C{=}C{-}CH_2-$ (with a CH_3 on the central carbon) possess but slight attraction for valence electrons as compared to groups with the vinyl configuration, $>C{=}CH-$. Therefore, it would be anticipated that in the rubber molecule the position of weakness, insofar as scission by heat is concerned, would be the bonds indicated below by dotted lines:

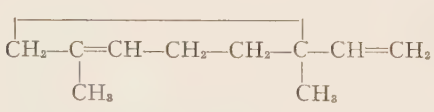


Complete scission into units of five carbon atoms would give the residue:  , which would appear as isoprene,  . Scission into units of ten carbon atoms would give the residue:

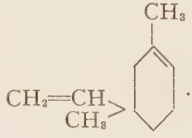


Readjustment of the bonds would provide several possibilities. For an adjustment, however, not involving migration of hydrogen atoms, a cyclic structure must result, in which case a 6-membered ring is most probable. For such a ring to be produced, the union must occur either between atoms 1,6 or atoms 3,8.

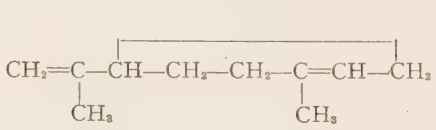
For 1,6 ring-closure:



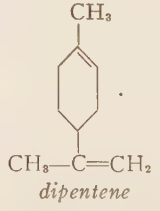
or



For 3,8 ring-closure:



or



dipentene

The latter of these two possibilities is apparently favored in practice. Admittedly, much of this exposition is speculative, but it has the merit

of furnishing a very satisfactory picture of the formation of isoprene and dipentene from rubber.

Midgley has made the most exhaustive recent study of the products of destructive distillation of natural rubber. In this work,[44a] he heated 200 pounds of light pale crêpe in 16 pound lots at atmospheric pressure and without any particular attention to temperature control, it having been determined that the more rapidly the rubber was destructively distilled the higher the yield of isoprene. Isoprene was the particular objective in this case. Iron retorts were used, and a gas flame was employed. After the removal of the bulk of the isoprene by fractionation, the residual oil was subjected to very thorough fractional distillation by special methods to separate the components. In addition to the liquid fractions, a substantial proportion of the original material was observed to polymerize during fractionation. This remained as a jelly in the distilling flask. Midgley assumes that these materials consisted very largely of dienes which were too unstable to permit of distillation.

The products of distillation were found to consist of olefines, dienes, aromatics, hydroaromatics and a single dicyclic olefine. No saturated compounds were detected. The list of the substances which were positively identified follow: methyl-3-butene-1; methyl-2-butene-1; isoprene; methyl-2-butene-2; a component of boiling point 59-60°; methyl-3-pentene-2; a component of boiling point 76-79° (this is considered to be a mixture of methyl-3-pentene-2, benzene, and methyl-3-pentadiene-2,4 but evidence is not clinching as yet); benzene (only 2 cc. of purified material); a component of boiling point 93-95° which is still unidentified; tetrahydrotoluene-delta-3; tetrahydrotoluene-delta-2 (very small amounts); a component of boiling point 109-110°; tetrahydrotoluene-delta-1; toluene; component of boiling point 121-122° which is considered to be a 2-methyl heptene; dihydro-*m*-xylene (probably delta-1,3); *m*-xylene; (no trace of *o*- or *p*-xylene); small amount of a component boiling point 140-141°; *p*-methylethyltetrahydrobenzene; a component of boiling point 151-153° in small amounts; thujene; *p*-ethyltoluene; a relatively large cut of a component boiling point 162-163° with an empirical formula of $C_{10}H_{18}$; dipentene. These compounds all seem to have been definitely identified, and Midgley has made the assumption similar to that above that the long chain structural formula for rubber hydrocarbon is broken at single valences to give a section containing the desired number of carbon atoms. He represents the points of breakage as partial valences, and resolves the double bonds into the partial valence form. The compounds enumerated above may

[44a] T. Midgley, Jr., private communication, 1928.

then be explained very readily, by making a few assumptions; namely, (1) that adjacent partial valences may unite to form stable double bonds; (2) that single partial valences, 6 carbons apart, may unite to form six-sided rings; (3) that any pair of partial valences may accept hydrogen if hydrogen is available; (4) that hydroaromatics can dehydrogenate to yield the corresponding aromatic; (5) that partial valences, not adjacent to other partial valences, may migrate in some cases.

It is rather significant that *m*-xylene is the only predictable ring compound of the aromatic series with 8 carbons, and that the *o*- and *p*-isomers were definitely absent. Benzene cannot, of course, be explained by simple mechanism, but the fact that other aromatics are present is sufficient explanation to account for the small amount of benzene isolated since benzene is more stable than other simple aromatic hydrocarbons.

Another interesting observation of this investigation is that if magnesium turnings (such as are used in Grignard reactions) are distributed through 16 pounds of pale crêpe prior to distillation, the yield of isoprene and dipentene, on pyrolysis, remains about the same as when magnesium was absent. The quantity of other hydrocarbons, however, is found to increase over 12-fold. The 16 pounds of rubber (with magnesium) produce about the same quantity of the latter as had been obtained from 200 pounds of rubber alone. Analysis of the products proved them to be the same as those already mentioned from rubber alone, but in different relative proportions. The aliphatic substances decreased; the aromatics increased; and the hydroaromatics remained nearly the same. Zinc, iron, aluminum and brass are somewhat less effective than magnesium, and copper appears to be without effect.

Rubber may be heated [45] in the absence of air at vulcanization temperatures (to 141°) for 8 hours with no drop in the chemical unsaturation, but at higher temperatures (245-360°) there is an isomerization to a substance with less unsaturation. The amount of lowering of the unsaturation depends on the time and temperature, a fact which was also noted by Staudinger.[46] If rubber is heated dry at 163°, or in solution at 80°, it yields only one polymer,[47] which is soluble in benzene and which differs from the benzene-soluble component obtained from untreated rubber. This softens at 185-200°, and decomposes at 250-260°. Concerning the polymerization of isoprene, etc., see page 735.

Rubber has a softening point,[48] resembling a melting point, and mere

[45] Fisher and Gray, *Ind. Eng. Chem.* **18**, 414 (1926).
[46] Staudinger and Geiger, *Helv. Chim. Acta* **9**, 549 (1926).
[47] Bruson, Sebrell and Calvert, *Ind. Eng. Chem.* **19**, 1033 (1927).
[48] Geiger, *Gummi-Ztg.* **40**, 2143 (1926); *Chem. Abstracts* **20**, 3165 (1926).

fusion involves no change in the double bonds. The softening point of Para rubber, for example, before and after mastication is 130-140° and 100-110° respectively. If the heating is performed in a vacuum instead of in air, these values become 210-220° and 120-130° respectively. Rubber starts to decompose in a vacuum at 250° with the disappearance of double bonds, forming "cyclo-rubber", an isomer with half the number of double bonds. In "polycyclo-rubber", only one double bond remains for four isoprene nuclei. This substance may be produced in 50 percent yield by long heating in a vacuum at 300-320°. Simultaneously, compounds of low molecular weight distil. According to Geiger, the thermal decomposition of rubber takes place in two steps, one beginning at about 300° and the second at 335-345°. In the first step, the distillate consists of isoprene, dipentene, and 20 percent of a high boiling oil, whereas the second step gives no dipentene, a little isoprene, and about 60 percent of the high boiling oil. Distillation experiments lead Staudinger and Geiger to believe that when rubber is heated, the extremely large molecules (macro-mols) decompose either into residues of 25-50 isoprene units, which in turn form polycyclo-rubber, or they decompose into smaller residues which form isoprene, dipentene and sesquiterpenes.

If rubber is reduced to hydro-rubber (saturated), and if this is heated to 350-400° at atmospheric pressure, there results [49] about 1 percent by weight of methyl-2-butene-1. Just as caoutchouc is derived from isoprene, so hydrorubber is considered to be derived from methyl-2-butene-1. Staudinger and Fritschi noted that the hydrorubber distilled at a more elevated temperature than rubber, but that the distillation was more complete. Only a small residue remained in the flask. From 80 grams there was 74 grams of distillate, of which at 4 mm. pressure 10.1 percent boiled at 55-75°; 6.1 percent at 75-100°; 16.9 percent at 150-220°; 17.6 percent at 220-270°; 22.3 percent at 270-315°; and 24.3 percent at 315-320°. The substances in the various fractions vary from C_5H_{10} to $C_{50}H_{100}$.

Staudinger [50] obtained a "cyclorubber" from rubber-hydrochloride, zinc, and hydrogen chloride in toluene. On heating, it decomposes into a mixture of hydrocarbons, but contrary to the results with rubber, no dipentene is isolable in the 165-180° (1 atmosphere) fraction. It was found that rubber heated *in vacuo* at 300° becomes transformed into a residue of cyclorubber, and a distillate amounting to 20 percent of the rubber, which contains about 60 percent of dipentene. It contains in

[49] Staudinger, *Ber.* **57**, 1203 (1924).
[50] Staudinger, *Z. angew. Chem.* **38**, 226 (1925).

addition, isoprene and polyterpenes. More vigorous heating (about 350°, *in vacuo*) induces the decomposition of the cyclorubber residue. By rapid distillation of rubber at higher temperatures, 95 percent distils, giving, among other things, methane, isoprene, and "iso-rubber".

A patent [51] relative to the production of dipentene from waste crude rubber scrap, or from vulcanized rubber, gives the following details. The material is heated in a still below 350° and below 2 atmospheres, until one-half to one-third of the charge is vaporized. The liquid distillate is stated to be mainly crude dipentene, and an increase of pressure lowers the yield of the dipentene. The gases of the reaction are used to heat the stills.

"Cyclopentadiene rubber", a polymerized product of cyclopentadiene,[52] begins to char above 160° with the evolution of yellowish vapors, and above 220° decomposes into gaseous products containing small amounts of cyclopentadiene. By condensing the gases, it was shown that unsaturates were present, but that no derivatives of acetylene were present.

[51] Bamber, Brit. 235,380, June, 1924. *Chem. Abstracts* **20**, 1004 (1926).
[52] Bruson with Staudinger, *Ind. Eng. Chem.* **18**, 382 (1926).

CHAPTER 6.

HALOGEN COMPOUNDS AND INORGANIC ESTERS.

Alkyl Halides.

As compared with most alkyl halides, methyl chloride is very stable towards heat. There is no indication [1] of decomposition below 420-425°, but at this temperature pyrolysis sets in and is quite noticeable at 495-500° C. In this work, dry methyl chloride was passed through a glass tube heated in an oil bath. Dumas and Peligot [2] had previously reported that dry methyl chloride is completely decomposed into hydrocarbon gases, carbon and hydrogen chloride when it is passed through a porcelain tube heated to cherry redness. Methyl chloride decomposes above 500°, and this decomposition is nearly complete [2a] at 900° as determined by the hydrogen chloride produced. At the high temperature, naphthalene is a product of the reaction.

Methyl iodide, although the most stable alkyl iodide, is decomposed somewhat [3] in 6 hours if maintained at 270°. Methane and ethylene are formed, the ethylene content varying from 3 to 12 percent. Hydrogen iodide is not formed, but it is consumed in the production of methane. Iodine is liberated in this process. When methyl bromide is passed through a hot tube (400-600°) filled with pumice or chalk,[4] the products of the reaction are methane, hydrogen and carbon, but no ethylene.

Ethyl chloride does not decompose at 410°, but [5] at 510-530° it gives a 55.4 percent yield of ethylene. In the latter experiment 18.4 grams of ethyl chloride were heated 1.5 hours in a pumice-filled tube. Six hundred cc. of other gases was also collected. Similarly, from 22 grams of ethyl chloride at 560-600°, the gaseous products are 76.8 percent ethylene. Practically no change is observed in *ethyl bromide* at 425°, but when it is passed at a rate of 1 gram in 3 minutes through an empty glass combustion tube at 480-525°, it produces an 88.5 percent yield of ethylene. In addition, 30 grams of the bromide produces 500 cc. of saturated gas. Nef also performed similar experiments with a tube

[1] C. S. Marvel, University of Illinois, private communication, 1927.
[2] Dumas and Peligot, *Ann. chim. phys.* [2] **58**, 28 (1835).
[2a] Wiesler, *Chem. Ztg.* **52**, 182 (1928).
[3] Kahan, *J. Chem. Soc.* **93**, 132 (1908).
[4] Nef, *Ann.* **318**, 12 (1901); **298**, 229-277 (1897).
[5] Nef, *Ann.* **318**, 14 (1901).

filled with soda-lime (see p. 18). His interpretation of the results involves the assumption of the primary formation of an ethylidene radical, which then rearranges into ethylene. With no evidence to the contrary, however, it seems more direct to assume the primary formation of ethylene.

Barium chloride on pumice appears to accelerate [6] the formation of olefines from either ethyl or propyl halides, since at 400-450° ethylene or propylene may be formed quantitatively.

The fact that ethylene iodide may be formed [7] by passing *ethyl iodide* through a hot tube has been known for a long time. Aronstein reported its formation even at 230°, in accordance with the equation:

$$2C_2H_5I \longrightarrow C_2H_4I_2 + C_2H_6.$$

Ethyl iodide starts to decompose [3] at the boiling point of dimethylaniline (192°), and the increase of its dissociation is fairly regular to 280°. Above that temperature, there is a secondary decomposition, thought to be that of hydrogen iodide. Iodine forms in the tube at 280-305°, but traces of it may be identified even at 210°. By heating ethyl iodide in a sealed tube at 270° for 3-5 hours, the gaseous products are nearly pure ethane; at 254°, for 2.5 hours, the ethane is contaminated with 25.5 percent of ethylene, but if the heating is continued for 7 hours, the ethylene content is only 4.6 percent. Kahan's results with ethyl iodide and with other alkyl iodides are wholly in favor of a preliminary dissociation into hydrogen iodide and alkylene (or alkylidene). To demonstrate the presence of hydrogen iodide, which is rarely encountered when the iodides are heated alone, ethyl iodide was heated with it in the presence of silver chloride. This, with hydrogen iodide, liberated hydrogen chloride, which is comparatively inert towards ethylene.

The investigations of Aronstein [8] with the two *propyl bromides,* and of von Roozeboom [9] with *iso-* and *tertiary*-butyl bromides showed that these alkyl bromides pyrolyze at elevated temperatures into C_nH_{2n} and hydrogen bromide. Nef [5] showed that practically the calculated yield of propylene (3.8 liters instead of 3.96 liters from 20 grams of bromide) was obtainable from *n*-propyl bromide by passing it through a pumice-filled tube at 500°. In contrast to these results, the hydrogen bromide which is liberated from *iso*butyl bromide, or the HCl from the chloride, does recombine somewhat to form the tertiary butyl halides (over pumice at 500°). Thus, from 20 grams of *iso*butyl bromide, Nef isolated

[6] Brooks, *Chem. Met. Eng.* **22**, 629 (1920).
[7] Kopp, *J. pharm. chim.* [3] **6**, 110 (1844); Aronstein and Kramps, *Ber.* **13**, 491 (1880).
[8] Aronstein, *Rec. trav. chim.* **1**, 134 (1882).
[9] von Roozeboom, *Ber.* **14**, 2396 (1881).

15 grams of tertiary butyl bromide after the pyrolysis, and from 20 grams of the chloride, he isolated 4 cc. of the tertiary isomer. In the latter case, 3.6 liters of butylene (mostly, but not entirely, *iso*butylene) was collected. From tertiary butyl chloride, at 400-500° over pumice, the only product of decomposition is *iso*butylene and hydrogen chloride. *Iso*butylene prepared in this manner, or better if passed over hot soda lime, is free from isomeric butylenes as impurities. At 570° over pumice, the *iso*butylene appears to undergo an incipient decomposition into methane, hydrogen and propylene. There is also some charring.

Both *n*- and *iso*-propyl iodides, when heated alone at 175-250° from 2 to 6 hours, suffer pronounced decomposition, much more than is true with ethyl iodide. The gaseous product, exclusive of a little hydrogen iodide, is nearly pure propane (99 percent propane and 1 percent hydrogen). Propylene is absent. One means of producing propylene in this reaction is to carry out the decomposition [3] in the presence of zinc, in which case about half of the gas is propylene. Zinc also augments the quantity of ethylene from ethyl iodide.

With proper temperature control, it is feasible to produce isomerization in alkyl halides by heat. It is ordinarily considered that an olefine and hydrogen halide are intermediate products, with the hydrogen halide recombining with the olefine in two different ways. This process has been summarized by Lucas and Jameson [10] as follows. "The rearrangement of an alkyl bromide when heated may be considered as taking place in two steps; first, the bromide dissociates into hydrogen bromide and alkylene, and second, the products recombine to form the isomeric alkyl bromide. The bromine goes to the more positive carbon atom, which in accordance with the idea of electron displacement is the one to which the most alkyl groups are attached. It should be a general rule that primary bromides will rearrange to give isomers in which the bromine is joined to the second carbon atom, and that these isomers will in turn rearrange to give tertiary derivatives, when the third carbon atom is tertiary". To illustrate with *n*-propyl bromide, the steps become

$$CH_3—CH_2—CH_2Br \longrightarrow HBr + CH_3—CH{=}CH_2 \longrightarrow CH_3—CHBr—CH_3$$

The polarity formula of propylene, which becomes the basis for the selection of the "more positive carbon atom", is determined by assuming, as Lucas does, that hydrogen radical is more electronegative than methyl (see p. 31). Thus, the electrons of the double bond are attracted towards the hydrogen and away from the methyl, leaving the central carbon atom the more positive one. This may be represented

[10] Lucas and Jameson, *J. Am. Chem. Soc.* **46**, 2479 (1924).

by the two types of formulas: $H_3C{:}CH \begin{matrix}\cdot\\ :\\ \cdot\end{matrix}CH_2$, or $H_3C^{+}\text{-}CH^{+}_{-}\text{-}CH_2$. For an intelligent application of such a principle, it must be kept in mind that this is merely a tendency which should lead to a preponderance of one isomer over the other rather than a total exclusion of the less favored isomer.

Some cases have already been cited to illustrate this principle. Others follow. At 280°, *n*-propyl bromide [11] forms some *iso*propyl bromide, and at 230° *iso*butyl bromide [12] yields tertiary butyl bromide. The conversion data for *n*- to *iso*-propyl bromide [13] are given in the table.

TABLE XVII. *Conversion of n-Propyl Bromide to Iso-Propyl Bromide.*

	In the Liquid State		In the Gaseous State	
Temperature	Hours	Percent Rearranged	Hours	Percent Rearranged
184°	2.5	3.27	7	7.24
	6	8.49		
237°	1.5	17.69	1	28.1
			7	35.12
262°	0.5	19.15	1	30.89
	1	21.79	2	34.45

The reverse change, that of *iso*- to *n*-propyl bromide, is much smaller. It reaches a value of only 2.39 percent after 3 hours at 262° in the liquid state, and 4.95 percent after 2 hours in the gaseous state. If either *n*- or *iso*-propyl bromide [14] is heated in the gaseous state, an equilibrium mixture of the two bromides results, together with some hydrogen bromide and propene. At 360°, the ratio of $iso/n = 73/27$.

Secondary butyl bromide [15] is perfectly stable at 140°, even after several hours heating. A 3 percent conversion of *iso*- into tertiary butyl bromide is induced [16] by heating the former for 30 hours in sealed tubes at 92-95°. The reaction proceeds [17] 15 times faster at 110°. When heated by xylene vapor at 140°, there is as much as 56 percent conversion in one hour, and the velocity of the rearrangement is much greater in a tube of 6 mm. diameter than in a tube of smaller bore (2 to 3.5 mm.). A limiting value of 72-74 percent tertiary butyl bromide is reached in 15 hours. This same value is held at 25 hours, and it is not changed materially at 184° or at 262° (*iso*amyl benzoate vapors).

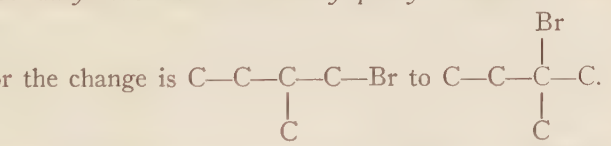
Obviously, if there is a limiting value in these rearrangements, this

[11] Aronstein, *Ber.* **14**, 607 (1881); **16**, 391 (1883).
[12] Eltekoff, *Ber.* **8**, 1244 (1875).
[13] Brunel, *Ann.* **384**, 245 (1911).
[14] Brunel and Rafsky, *Science* **60**, 23 (1924).
[15] Lucas, Simpson and Carter, *J. Am. Chem. Soc.* **47**, 1468 (1925).
[16] Michael and Leupold, *Ann.* **379**, 263-332 (1911). A good summary of previous work is given here.
[17] *Ibid.*, p. 306.

value should be approachable from either side. Actually, the reverse process, namely, the conversion of tertiary butyl bromide to *iso*butyl bromide has also been investigated at various temperatures. In 10 hours at 110°, there is less than 0.5 percent conversion; in 11 hours at 184°, there is but 3.5 percent, and after 35 hours only 7 percent. At 262°, however, the limiting value is approached quite rapidly, 13.8 percent of the *iso*- being formed in 15 minutes, and 26.3 percent in two hours. The conversion of either the *iso*- or the tertiary butyl bromide is found to be much more rapid in the liquid state than in the gaseous at corresponding temperatures. For example, a mixture of 73 percent tertiary and 27 percent *iso*-butyl bromides does not change materially if heated in the liquid state up to 237°, but if heated in the gaseous state at 237°, the percentage of the tertiary compound increases to 87.89 percent after 10 hours. Brunel,[18] working at 280°, found that the equilibrium value of tertiary butyl bromide in the iso-tertiary mixture is between 90 and 91 percent, and according to him,[13] the velocity of the transformation, particularly that of *iso*butyl bromide, is catalytically influenced by the degree of cleanliness of the walls of the vessel, and also by the presence of the liquid phase.

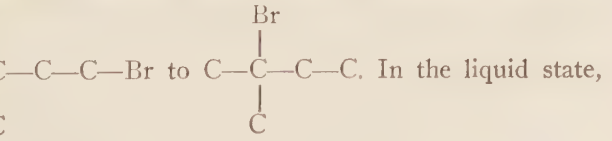
For the amyl bromides, the conversion values are given in the work of Michael and Leupold.[19] Here also, the values in the liquid state are quite different from those in the gaseous state.

(*a*) *From active amyl bromide to tertiary pentyl bromide.* The skeleton formula for the change is



In the liquid state, there is 18.8 percent conversion in 2 hours at 184°; 28-30 percent in half an hour at 237°; and 48 percent in half an hour at 262°. In the gaseous state, the rate of conversion is slower at 184°, but is more rapid at 237°. Thus, in one hour at 184°, there is about 1 percent rearrangement, and in 7 hours about 9 percent, whereas in half an hour at 237° the value is 47-51 percent.

(b) *From isoamyl bromide to tertiary pentyl bromide.* The skeleton change is

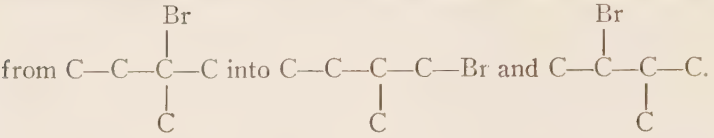


In the liquid state,

[18] Brunel, *Ber.* **44**, 1000 (1911).
[19] Michael and Leupold, *Ann.* **379**, 326-332 (1911).

this change only occurs to the extent of about 1 percent at 262°. From the principle expounded on p. 127 a larger value would have been anticipated, and possibly this would be attainable in the gaseous state.

(c) *From tertiary pentyl bromide into isomeric substances.* At 184°, there is a 7 percent conversion in 30 minutes into active amyl bromide, and about 12 percent into methyl *iso*propyl bromomethane, by heating in the liquid state. These skeleton changes are



(d) *From methyl isopropyl bromomethane into tertiary pentyl bromide.* In this case, there is 5-8 percent conversion in the liquid state at 184° (6 hours), and 12-19 percent at 237° in 15 minutes.

(e) *From 2,2-dimethyl-1-bromo-propane, $(CH_3)_3C—CH_2Br$, into tertiary pentyl bromide.* In this case,[20] there is an apparent interchange of methyl with bromine. The transformation is rapid by distillation, and the same is true with the iodide. The chloride is more stable, but it also gives the same reaction in part. In addition there is a partial elimination of hydrogen chloride with the formation of trimethyl ethylene. The reader is referred to Michael's original papers for the theoretical developments of these data. A concise summary is presented in Henrich's "Theories of Organic Chemistry", translated by Johnson and Hahn, New York, John Wiley & Sons, Inc., **1922,** p. 581.

α-Bromo-acids and esters will be touched briefly because of their relationship to the alkyl halides. Later they will be given in more detail. Ethyl α-bromobutyrate boils at 177°; it is less than 1.5 percent converted into the β-isomer by repeated distillation.[21] Ethyl α-bromo*iso*-butyrate is only changed to a slight extent by 2 hours of refluxing. α-Bromo*iso*butyric acid is not transformed into the β-acid at 100°, and α-bromopropionic acid may be distilled unchanged at atmospheric pressure. If the latter is heated for several hours in a sealed tube at 120-130°, it yields a small amount of the β-isomer.

In monomolecular transpositions, such as that of *iso*butyl bromide into tertiary butyl bromide, Ramart-Lucas believes[22] that the reaction does not proceed by a dissociation process, but rather regards every atom in the compound as being constantly attached to the rest of the molecule by at least one electron. Such an internal readjustment may

[20] Tissier, *Ann. chim. phys.* [6] **29,** 358-363 (1893).
[21] Michael, *Ber.* **34,** 4035 (1901).
[22] Ramart-Lucas, *Compt. rend.* **185,** 561 (1927); **186,** 39 (1928).

be caused either by heat, by radiation such as ultraviolet rays from a mercury lamp, or by catalysts.

Prevost [22a] has pointed out the following relationship of an α-unsaturated bromide into a β-isomer, which takes place at about 70°:

$$\begin{matrix} R{-}C{=}CH{-}CH_3 \\ \quad | \\ \quad Br \end{matrix} \longrightarrow R{-}CH{=}CH{-}CH_2Br\,.$$

Dihalogen Compounds.

As might be anticipated, methylene iodide is more stable towards heat than ethylene iodide. The former boils at 180° with some decomposition; the latter evolves iodine [23] at 50-60°. Further experimental work may reveal that the iodine comes from hydrogen iodide, which is the logical product of pyrolysis. In contrast to ethylidene chloride, which decomposes [24] at 300° and above into hydrogen chloride and vinyl chloride, ethylidene bromide forms an equilibrium mixture at 300-315° with its isomer [25] ethylene bromide. With the chlorides, this constitutes an excellent method of preparation for monochloroethylene. At 300-400°, the dichlorides are in varying equilibria with their decomposition products, the amount of the latter formed increasing with the rise in temperature, but also varying with the extent of surface of the glass vessel. Above 400°, the decomposition into chloroethylene is complete. Vinyl chloride is thus conveniently synthesized by passing dichloroethane through a pumice-filled tube at dull red heat.[26] Ethylene dichloride also pyrolyzes into vinyl chloride and hydrogen chloride. The conditions stated are a nitrogen atmosphere and a temperature of 600°, following which the gas is washed with water, dried and liquefied. Vinyl chloride boils at — 18°.

$$C_2H_4Cl_2 \longrightarrow CH_2{=}CHCl + HCl\,.$$

The propylene bromides, and trimethylene bromide, pyrolyze at 240-250° in accordance with the following equilibria,[27] after a few hours' heating:

$$\begin{matrix} CH_2Br \\ | \\ CH_2 \\ | \\ CH_2Br \end{matrix} \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2Br \\ + HBr \end{matrix} \rightleftharpoons \begin{matrix} CH_3 \\ | \\ CHBr \\ | \\ CH_2Br \end{matrix} \rightleftharpoons \begin{matrix} CH_3{-}CBr{=}CH_2 + HBr \rightleftharpoons CH_3{-}CBr_2{-}CH_3 \\ CH_3CH{=}CHBr + HBr \rightleftharpoons CH_3CH_2CHBr_2\,. \end{matrix}$$

[22a] Prevost, *Compt. rend.* **185**, 1283 (1927).
[23] Regnault, *Ann.* **15**, 67 (1835).
[24] Biltz, *Ber.* **35**, 3524 (1902). Biltz and Küppers, *Ber.* **37**, 2398 (1904).
[25] Sokownin and Zinewsky, *Ann.* **354**, 354 (1907).
[26] Boeseken and Bastet, *Rec. trav. chim.* **32**, 184 (1914).
[27] Sokownin, *Ann.* **354**, 358 (1907).

A similar complex equilibrium is encountered in the case of dibromo-*iso*butane. In this case, even a lower temperature (210-225°) will induce the change. Dihalogen compounds, containing an aromatic radical, shall be mentioned later.

Hill and Tyson have studied the action of heat (360° to 470°) and soda-lime on 1,1-dichloroheptane, in an effort to produce heptyne-1. Because of rearrangements,[28] however, the yields of the acetylene homolog were poor (2 to 10 percent).

In attempting to distil the hydrochlorides of isoprene, Bouchardat [29] found that a solid residue was obtained which had the properties of rubber, and this rubber represented about one-sixth of the weight of the isoprene used. It was very difficult to eliminate the last traces of chlorine.

Compounds Containing Three or More Halogens.

A comparison of the behavior of chloroform, bromoform, carbon tetrachloride, carbon tetraiodide, and hexabromo-ethane towards heat shows that in each case, the chief reaction is the formation of an unsaturated compound. Carbon tetraiodide undergoes decomposition as low as 120°, whereas the tetrachloride is stable to 600°. If carbon tetrachloride is passed [30] through a quartz tube at 1300-1400°, the yield of tetrachloroethylene which is thereby produced is 80 percent.

$$2CCl_4 \longrightarrow 2Cl_2 + Cl_2C{=}CCl_2.$$

In this reaction, the product must be cooled rapidly to prevent the formation of hexachloroethane. At 900-1000°, the yield of tetrachloroethylene is 43 percent. In the electric arc, carbon tetrachloride decomposes into carbon and perchlorobenzene.[31]

If the vapors of chloroform are decomposed by a platinum wire,[32] whose estimated temperature is 1000°, tetrachloroethylene is also the chief product:

$$2CHCl_3 \longrightarrow 2HCl + C_2Cl_4.$$

The by-products are hexachloroethane and hexachlorobenzene. Under similar circumstances, bromoform pyrolyzes chiefly into tetrabromoethylene. By distilling trichloro-iodomethane, there is a partial decomposition [33] into iodine and hexachloroethane. The decomposition of heptachloropropane and of octachloropropane apparently pursue differ-

[28] Hill and Tyson, *J. Am. Chem. Soc.* **50**, 175 (1928).
[29] Bouchardat, *Compt. rend.* **89**, 1117 (1879).
[30] Weiser and Wightman, *J. Phys. Chem.* **23**, 415 (1919).
[31] Schall, *Chem. Abstracts* **4**, 2276 (1910).
[32] Loeb, *Z. elektrochem.* **7**, 903 (1901); Joist and Loeb, *ibid.* **11**, 938 (1905).
[33] Besson, *Compt. rend.* **115**, 1078 (1892).

ent courses. The latter,[34] at 300°, gradually breaks down into carbon tetrachloride and tetrachloroethylene, whereas heptachloro-propane gives [35] hydrogen chloride and hexachloro-propylene in yields ranging from 1.3 to 62.3 percent, at temperatures between 240-420°. There appears to be no formation of chloroform and tetrachloroethylene.

In conformity with the stability of unsaturated halogen compounds, it is interesting to record [36] that hexachlorobutadiene, $CCl_2{=}CCl{-}CCl{=}CCl_2$, is quite thermostable. It boils almost without decomposition at 269° or 284°. It is in keeping with other data on iodides that tetraiodoethylene would be less stable than tetrachloroethylene. By heating [37] in different solvents, it gives the following equilibrium:

$$C_2I_4 \rightleftharpoons C_2I_2 + I_2.$$

In addition, the diiodo-acetylene [38] changes in the following manner by heating with water in a sealed tube on the water bath for 30 minutes:

$$2C_2I_2 \longrightarrow C_2I_4 + 2C.$$

This is a simultaneous oxidation and reduction, which is reminiscent of the change of carbon monoxide into carbon dioxide and carbon. Without the presence of water, diiodoacetylene [39] undergoes an explosive reaction in a sealed tube at 81-100°, giving iodine and carbon.

α,β,β'-Trichlorodiethyl sulfide,[40] $CH_2Cl{-}CHCl{-}S{-}CH_2{-}CH_2Cl$, behaves merely as a halogen derivative when heated. Hydrogen chloride is detached, even by distillation at 3.5 mm., thereby producing a mixture of β-chloroethyl-β-chlorovinyl sulfide and β-chloroethyl-α-chlorovinyl sulfide. By refluxing $\alpha,\beta,\beta,\beta'$-tetrachlorodiethyl sulfide for 14 hours at 150-160°, β-chloroethyl-β,β-dichlorovinyl sulfide results:

$$Cl_2CH{-}CHCl{-}S{-}CH_2{-}CH_2Cl \longrightarrow HCl + Cl_2C{=}CH{-}S{-}CH_2{-}CH_2Cl.$$

A halogen derivative of codein, namely, α-chlorocodide,[41] rearranges into β-chlorocodide by heating above its melting point. In this process there is some decomposition which may be avoided by heating the former for one hour in boiling bromobenzene. The yield is 70-75 percent, and this value drops to 50 percent if boiling tetralin is used.

[34] Krafft and Merz, *Ber.* **8**, 1298 (1875).
[35] Boeseken, van der Scheer and de Groot, *Rec. trav. chim.* **34**, 78 (1915).
[36] Krafft, *Ber.* **10**, 801 (1877); Hartmann, *Ber.* **24**, 1022 (1891); Hoffmann, *Ber.* **22**, 1270 (1889).
[37] Schenk and Litzendorff, *Ber.* **37**, 3456 (1904).
[38] V. Meyer and Pemsel, *Ber.* **29**, 1411 (1896).
[39] Nef, *Ann.* **298**, 347 (1897).
[40] Lawson and Dawson, *J. Am. Chem. Soc.* **49**, 3119, 3125 (1927).
[41] Speyer and Rosenfeld, *Ber.* **58**, 1113 (1925).

Iodide-chlorides.

Methyl iodide-chloride,[42] CH_3ICl_2, decomposes at $-28°$; in water, it changes into methyl chloride and ICl. Iodochloride-2-chloro-ethylene, $CHCl{=}CHI.Cl_2$, spontaneously liberates[43] iodine monochloride, and trichloro-iodo-ethane (40 percent yield); and much lesser yields of symmetrical-tetrachloroethane and of dichloro-diiodo-ethane, $CHCl_2CHI_2$ (less than 10 percent). Similarly,[44] iodochloride-2-iodo-1-dichloro-1,2-ethene, $ClIC{=}CClI.Cl_2$, yields iodine monochloride, symmetrical diiodo-dichloro-ethylene, $ClIC{=}CClI$, and triiodo-chloro-ethylene as well as some trichloro-iodo-ethylene and iodine trichloride. Howell gives the following explanation of this reaction. Two unsaturated residues, Cl—CH—CH—I and Cl—CH—CH—Cl, remain after the elimination of Cl_2 or of ICl. Then, it is a question of recombination of these factors. Since $CHCl_2$—CHClI can be formed either by CHCl—CHI + Cl_2 or by CHCl—CHCl + ICl, it would be anticipated in large amounts. With the other iodochloride, namely, iodochloride-1,2-dichloro-2-iodo-ethylene, the same course is advocated: $ClIC{=}CCl{-}I{<}^{Cl}_{Cl}$ and $ClIC{=}CCl{-}\overset{I{-}Cl}{\underset{Cl}{\vdots}}$, but since hexachloroethane is the only saturated compound formed, this indicates the extreme non-reactivity of ClIC=CICl and $ClIC{=}CCl_2$. With this explanation, it is necessary to postulate replacement of chlorine by iodine (giving $ClIC{=}CI_2$), and of iodine by chlorine (giving C_2Cl_6).

When dichlorovinyl-phenyliodonium bromide,[45] C_6H_5—I(Br)—CCl=CHCl, is heated at 180°, it undergoes decomposition into phenyl iodide and ClCH=CClBr. Phenyl iodide-chloride undergoes a sudden decomposition between 110-136°, chiefly in accordance[46] with the following equation:

$$C_6H_5ICl_2 \longrightarrow p\text{-}Cl{-}C_6H_4{-}I + HCl.$$

This is particularly true if it is heated rapidly. The amount of chlorine which is liberated as such never exceeds 27 percent of the theoretical.

[42] Thiele and Peter, *Ber.* **38**, 2845 (1905).
[43] Howell, *J. Am. Chem. Soc.* **45**, 182 (1923).
[44] Howell with Noyes, *J. Am. Chem. Soc.* **42**, 991 (1920).
[45] Thiele and Umnoff, *Ann.* **369**, 147 (1909).
[46] Caldwell and Werner, *J. Chem. Soc.* **91**, 528 (1907).

However, *p*-iodonitrobenzene dichloride, $O_2N—C_6H_4—ICl_2$ gives free chlorine entirely at 173°. The *meta* isomer decomposes at 103°, giving 28 percent of substitution (*m*-chloronitrobenzene); and *p*-iodo-chlorobenzenedichloride, $ClC_6H_4ICl_2$, gives 27 percent of substitution at 112°.

Acetylene Derivatives.

Diiodoacetylene has already been mentioned. Monochloroacetylene is very unstable.[47] It can be handled only when diluted with hydrogen. It changes into carbon and hydrogen chloride. The corresponding iodine derivative is unknown. Its homolog, $CH_3—C{\equiv}C—I$, is a liquid that boils without decomposition at 110°. Howell and Noyes[44] advance reasons for preferring the structures, $IC{\equiv}CI$ and $HC{\equiv}CI$, as opposed to $I_2C{=}C$ and $IHC{=}C$, suggested by Nef.[48]

Aromatic Compounds with Halogens in the Side Chain.

Mono-halogen Compounds.

In general there is elimination of HX from compounds of this type as from the simpler derivatives. Thus, *o*-γ-chloropropyl benzanilide loses hydrogen chloride vigorously at 200°;

$$C_6H_5CO—NH—C_6H_4—CH_2CH_2CH_2Cl \longrightarrow HCl + C_6H_5CONH—C_6H_4—CH_2CH{=}CH_2.$$

If the experiment[49] is performed in a vacuum, a 50 percent yield of *o*-allyl benzanilide (boiling point (12 mm.) 235-240°) results. Furthermore, benzoyl chloride and tetrahydroquinoline are in the distillate. Benzalacetophenone is readily prepared by heating[50] the compound, $C_6H_5COCH_2CHClC_6H_5$. Another illustration is the transformation[51] of resorcinol bis-(γ-bromopropyl) ether into resorcinol diallyl ether by heating above 225-230°. The decomposition is complete, in accordance with the equation:

$$1,3\text{-}C_6H_4(O—CH_2—CH_2—CH_2Br)_2 \longrightarrow 2HBr + C_6H_4(O—CH_2—CH{=}CH_2)_2$$

This pyrolysis starts at considerably lower temperatures. It is quite probable that another reaction would be encountered, namely, the rearrangement of the anticipated ether into diallyl resorcinol, unless fairly low temperatures are maintained. This matter is taken up on p. 227.

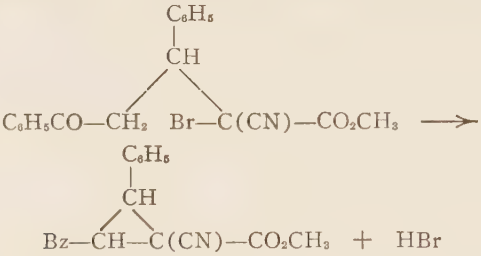
Although this is the customary reaction, there are other possibilities which are sometimes found in practice. Thus, in the distillation of

[47] Wallach, *Ann.* **203**, 91 (1880).
[48] Nef, *Ann.* **298**, 355 (1897).
[49] von Braun and Steindorff, *Ber.* **37**, 4726 (1904).
[50] Claisen and Claparede, *Ber.* **14**, 2465 (1881).
[51] Wilson with Adams, *J. Am. Chem. Soc.* **45**, 533 (1923).

1,1-diphenyl-2-chloroethane, stilbene is reported [52] to be formed in quantitative yields:

$$(C_6H_5)_2CH{-}CH_2Cl \longrightarrow C_6H_5CH{=}CHC_6H_5 + HCl.$$

In this reaction there is not only hydrogen chloride elimination, but rearrangement as well. It is of interest to note that the rearrangement is towards greater symmetry. In the next case, hydrogen bromide is eliminated as would be expected, but a cyclopropane derivative, and not an ethylene derivative, is formed. The change comes by heating *in vacuo*.



The proof of the structure [53] of the cyclopropane derivative is based on the characteristic lack of both color and fluorescence of such cyclopropane derivatives; on its inability to reduce permanganate; and on the ease with which it absorbs two atoms of hydrogen (by zinc dust in methanol-methyl acetate) to form a saturated compound.

Benzyl chloride [54] and xylyl chloride [55] form anthracene and dimethyl anthracene respectively, when heated for several hours with about two volumes of water at 190-215°. No permanent pressure is developed in the reaction tubes. The reaction with benzyl chloride is interesting since it was the first synthesis of anthracene. There is also aldehyde formation due to the water, and furthermore, the fraction having the boiling point 275-280°, from which anthracene separates also contains a liquid hydrocarbon which pyrolyzes into anthracene and hydrogen on passing through a glowing tube. At least two possible mechanisms suggest themselves for the production of anthracene. Either "phenyl-methylene" is formed as an intermediate product with the elimination of hydrogen chloride, or *o*-benzyl benzyl-chloride is the intermediate product. There is evidence for both schemes. Thus, Nef [56] showed that when benzyl chloride is distilled at a temperature of 400-600° through tubes filled with pumice or chalk, about 25 percent of stilbene results and also a "phenylmethylene resin". He did not mention

[52] Hepp, *Ber.* **6**, 1439 (1873).
[53] Kohler, Graustein and Merrill, *J. Am. Chem. Soc.*, **44**, 2554 (1922).
[54] Limpricht, *Ann.* **139**, 308 (1866).
[55] van Dorp, *Ann.* **169**, 207 (1873).
[56] Nef, *Ann.* **318**, 12 (1901).

anthracene, but the presence of stilbene may be accounted for by the transitory presence of phenylmethylene, which, by its reactivity, may also have reacted in other ways. Loeb [57] also identified stilbene after passing benzyl chloride vapors over a red hot wire:

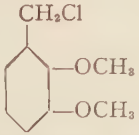
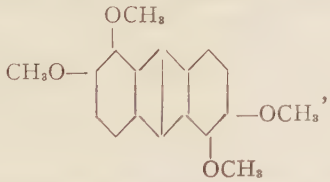
$$2C_6H_5CH_2Cl \longrightarrow 2HCl + C_6H_5CH{=}CHC_6H_5.$$

If, on the other hand, it is assumed that the primary change of benzyl chloride is to *o*-benzyl-benzyl-chloride, then the subsequent changes are to dihydroanthracene and anthracene:

$$C_6H_4\begin{<}{CH_2Cl}{CH_2{-}C_6H_5} \longrightarrow HCl + C_6H_4\begin{<}{CH_2}{CH_2}C_6H_4 \longrightarrow$$

$$HCl + H_2 + C_{14}H_{10}.$$

Zincke [58] reported the data of the latter reaction. During the vacuum distillation of *o*-benzyl-benzyl-chloride, hydrogen chloride is evolved and a resinous mass is left, which decomposed by heating at atmospheric pressure into anthracene and toluene. Some benzyl chloride and some benzyl toluene are also formed. Very similar results are obtained if the entire distillation is performed at atmospheric pressure. At bright red heat,[59] benzyl chloride has been found to decompose into toluene, stilbene, a trace of symmetrical diphenylethane, but no phenanthrene. Anthracene was not mentioned.

o-Veratryl chloride,  , may be distilled [60] at 11 mm. pressure at 129°, but at higher pressures an anthracene derivative, presumably  , is formed.

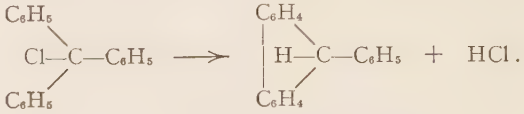
One of the best ways to prepare tetraphenyl-ethylene [61] is to heat diphenyl-bromomethane for an hour at 250-300°. The reaction proceeds very smoothly:

$$2(C_6H_5)_2CHBr \longrightarrow 2HBr + (C_6H_5)_2C{=}C(C_6H_5)_2.$$

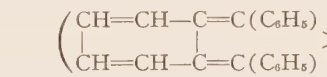
The stability of tetraphenylethylene to heat is witnessed by the fact that it boils at 415-425°. This compound is also formed when benzo-

[57] Loeb, *Ber.* **36**, 3059 (1903).
[58] Zincke, *Ber.* **7**, 276 (1874).
[59] Meyer and Hofmann, *Monatsh.* **38**, 141 (1917).
[60] Kaufmann and Müller, *Ber.* **51**, 123 (1918).
[61] Nef, *Ann.* **298**, 237 (1897). Staudinger and Endle, *Ber.* **46**, 1437 (1913).

phenone bromide, $(C_6H_5)_2CBr_2$, is distilled.[62] Triphenylchloromethane differs from the preceding compounds in having only aromatic hydrogens in the molecule. It undergoes pyrolysis [63] at 200°, forming 9-phenyl fluorene:



Another case which is similar [64] is that of phenylethynyl-diphenylchloromethane, $C_6H_5C{\equiv}C{-}C(C_6H_5)_2{-}Cl$. Here again, only aromatic hydrogens are present. This substance decomposes at 120° in the vacuum of the water pump with the evolution of hydrogen chloride, thereby producing a 25 percent yield of a red-orange hydrocarbon, rubrene, $C_{42}H_{28}$. Its structure is considered to be



To effect this change, two mols of hydrogen chloride must be removed from two of the original substance. Rubrene melts at 331°; its solutions are stable in the dark, but are oxidized and decolorized in the light by atmospheric oxygen. At 100-150°, rubrene peroxide changes quantitatively into rubrene and oxygen.

Di- and Poly-halogen Compounds.

The substances which have been considered have possessed one halogen atom to the molecule. *Benzal chloride,* with two halogens, decomposes [57] when it is passed over a red hot wire in much the manner of benzyl chloride since it forms a derivative of stilbene. The products of the reaction are a mixture of α- and β-tolane dichlorides:

$$2C_6H_5CHCl_2 \longrightarrow 2HCl + C_6H_5{-}CCl{=}CCl{-}C_6H_5.$$

Benzotrichloride is also broken down by the heated wire, and the products formed are tolane tri- and tetra-chloride; the tolane dichlorides are assumed by Loeb to be intermediate products. Benzophenone bromide has already been mentioned.

With a functional group such as $=CHBr{-}CHBr=$, it is fairly simple to eliminate one mol of hydrogen bromide by heat to give $=CH{=}CBr=$, but the removal of the second bromine to produce either an acetylene or an allene type of compound is extremely rare at the

[62] Friedel and Balsohn, *Bull. soc. chim.* **33**, 338 (1880).
[63] Hemilian, *Ber.* **7**, 1208 (1874); **11**, 202. 837 (1878). Fischer, *Ber.* **11**, 613 (1878); *Ann.* **194**, 257 (1878); Nef, *Ann.* **309**, 167 (1899); Schwarz, *Ber.* **14**, 1522 (1881).
[64] Moureau, Dufraisse and Dean, *Compt. rend.* **182**, 1440 (1926); Moureau and Dufraisse, *Z. physik. Chem.* **130**, 472 (1927); Moureau, Dufraisse and Enderlin, *Compt. rend.* **187**, 406 (1928).

lower temperatures and has been but little studied at the higher temperatures. It is known, however, that diphenyl-dichloro-ethylene, $(C_6H_5)_2C{=}CCl_2$, is quite stable [65] at high temperatures, more so than diphenyl ketene, $(C_6H_5)_2C{=}C{=}O$, which has a related structure.

In the case of 1,1,3-triphenyl-1,2-dibromo-propane,[66] one mol of hydrogen bromide is detached above the melting point, 94°.

$$(C_6H_5)_2CBr{-}CHBr{-}CH_2C_6H_5 \longrightarrow (C_6H_5)_2C{=}CBr{-}CH_2C_6H_5 + HBr$$

The dibromide of benzalpyruvic acid,[67] $C_6H_5CHBr{-}CHBr{-}CO{-}CO_2H$, loses HBr on heating, and this effect causes a fluctuation in the melting point from 125 to 142°. If the acid is boiled in water for ten minutes, β-bromobenzalpyruvic acid is formed.

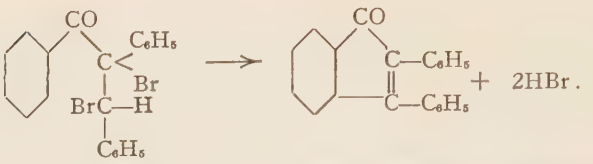
The method of synthesis for diaryl bromo-ethylenes which is customarily used [68] is the thermal decomposition of the corresponding dibromides. The temperature of the decomposition is so low that the isolation of the dibromides is a comparatively difficult matter in most cases. The simplest compound of this type, diphenyl-dibromo-ethane, is isolable. At its melting point, 63°, it pyrolyzes [69] into hydrogen bromide and diphenylbromoethylene:

$$(C_6H_5)_2CBr{-}CH_2Br \longrightarrow HBr + (C_6H_5)_2C{=}CHBr.$$

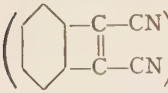
The latter may be prepared in 87 percent yield (Hurd and Webb) by heating a solution of the former in carbon disulfide. The syntheses of phenyl-α-naphthylbromo-ethylene, phenylanisylbromo-ethylene and phenyl-p-tolyl-bromo-ethylene (all of the type $Ar_2C{=}CHBr$) proceed by similar reactions with 87, 52, and 53 percent yields respectively. Either carbon disulfide or chloroform may be used as solvent for the dibromide during the pyrolysis. Phenylmethylbromo-ethylene cannot be prepared by this method, since the dibromide retains both bromine atoms even at 100° in a vacuum. From this it is obvious that the methyl group gives a degree of stability to the molecule; or, from another viewpoint, two aryl groups are essential for the facile elimination of HBr.

Both bromines are lost [70] during the heating (at 140-145°) of diphenyl-benzoyl-dibromo-ethane, but this is caused by the spatial proximity of an aromatic hydrogen atom which is also lost as a 5-membered ring is formed. Diphenyl indone is thus prepared in 89 percent yields:

[65] Staudinger and Endle, *Ber.* **46**, 1437 (1913).
[66] Ziegler, Richter and Schnell, *Ann.* **443**, 161 (1925).
[67] Reimer, *J. Am. Chem. Soc.* **48**, 2454 (1926).
[68] Hurd and Webb, *J. Am. Chem. Soc.* **49**, 550 (1927).
[69] Lipp, *Ber.* **56**, 569 (1923).
[70] Orékhoff, *Bull. soc. chim.* **25**, 597 (1919).

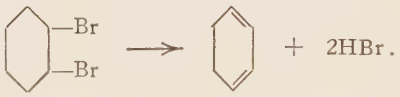


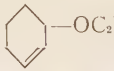
o-Di-bromocyanomethyl-benzene, NC—CHBr—C_6H_4—CHBr—CN, also loses [71] both halogen atoms merely by heating *in vacuo*. The structure, provisionally assigned to the substance which is formed, is



Alicyclic Halogen Derivatives.

Cyclohexadiene may be prepared [72] in about 25 percent yields by heating *cis*-cyclohexene-dibromide above its boiling point under pressure:

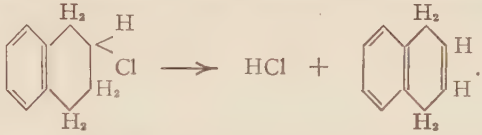


This reaction is interesting since alcoholic potassium hydroxide fails to give it, forming [73] instead the ether,  . Quinoline, however, may be employed to give fair yields of the diene. The *cis*-dibromide, mentioned above, boils with considerable decomposition at 220°. With the pressure of 800 mm., it boils at 230°, thereby destroying about half of it. In this process, part of it is converted into cyclohexadiene and part into a carbonaceous residue. It appears, however, that this carbonaceous residue is also encountered when the dibromide is merely left in sealed tubes.

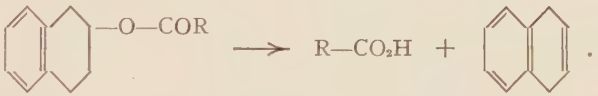
This ability of cyclohexene dibromide to change into cyclohexadiene is a simple case which is illustrative of a very general reaction, and one which has been used with singular success in the tetralin series. Tetralin (tetrahydronaphthalene) itself is very smoothly converted into naphthalene by heating the dibromide. Actually, it is not necessary to isolate the dibromide. According to the directions in Houben-Weyl,[74] which have been checked in the author's laboratory, bromine is slowly dropped into boiling tetralin which is contained in a distilling flask. The delivery tube of the flask is bent upwards at about the center and this is attached

[71] Challenor and Ingold, *J. Chem. Soc.* **123**, 2078 (1923).
[72] Greengard, Northwestern University, private communication.
[73] Crossley, *J. Chem. Soc.* **85**, 1415 (1904).
[74] Houben-Weyl, "Die Methoden der Organischen Chemie," Leipzig, Georg Thieme, 1922. Zweite Auflage, III, 865.

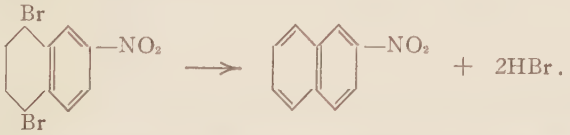
to an air condenser (vertical), from which hydrogen bromide passes, quite free from bromine. The purpose of the elbow in the delivery tube is to provide a small tetralin trap which reacts with traces of unused bromine that would otherwise escape. The yield of hydrogen bromide is about 90 percent of the theoretical on the basis of the total bromine used. This constitutes one of the most satisfactory methods for the preparation of *hydrogen bromide*. Naphthalene constitutes the end product in the flask, and this is, of course, valueless, relatively. Dihydronaphthalene may be prepared [75] by distilling β-chlorotetralin:



If this chloride is regarded as an ester, the decomposition of the following ester is a parallel case:



Reference has already been made (p. 90) to the pyrolysis of α- and particularly of β-substituted tetralin compounds to the corresponding naphthalene derivatives. A modification of this plan, and one which is more generally useful because of the lower temperatures employed, is based on the above debromination reaction. The dibromide of the substituted tetralin is prepared and heated; hydrogen bromide is eliminated and the substituted naphthalene remains. This is the best method of synthesis for β-nitronaphthalene,[76] and in this case also, it is not necessary to isolate the pure dibromide. It may be assumed that the two bromine atoms enter in the 1,4 positions:



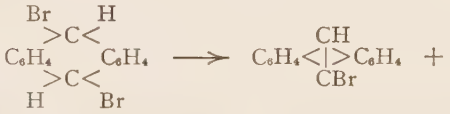
The yield of pure β-nitronaphthalene is 96-98 percent, if the heating is performed in a vacuum. Veselý [77] has prepared various bromonitronaphthalenes from the corresponding bromonitrotetralins, by the use of bromine at 100° until hydrogen bromide is no longer evolved, and then

[75] Bamberger and Lodter, *Ber.* **23**, 210 (1890).
[76] von Braun, Hahn and Seeman, *Ber.* **55**, 1687 (1922).
[77] Vesely and Chudozilov, *Bull. soc. chim.* **37**, 1436 (1925); *Chem. Abstracts* **19**, 3486 (1925); **20**, 382 (1926).

heating at 200° for an hour. The various isomeric bromonitronaphthalenes prepared by this method are: NO_2,Br = 1,2; 2,1; 3,2; 3,1; 1,3; and 2,4-dinitro-1-Br; and 1,3-dinitro-2-Br.

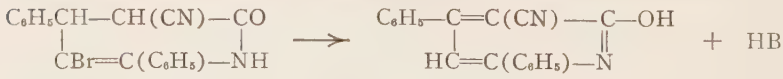
Almost a quantitative yield of *p*-diphenyl-benzene [78] (terphenyl) may be realized if 1,4-dicyclohexyl-benzene is treated at 160° with 12 atoms of bromine. The dicyclohexylbenzene is prepared in 60 percent yields by the Friedel and Crafts reaction with cyclohexyl bromide, benzene and aluminum chloride, so that this constitutes a very satisfactory synthesis of terphenyl. In one case which has been studied, namely, the dibromide of methyl-β-tetralyl ketone,[76] the elimination of hydrogen bromide is not smooth. The reason for this is not obvious, but it has been suggested that the two bromines may have substituted in 1,2 positions in the alicyclic nucleus instead of 1,4.

Pyrolysis of anthracene dibromide [79] leads to the formation of 9-bromo-anthracene:



This was taken as evidence that the dibromide was chiefly the *trans* form, with a little of the *cis* as impurity, since a small amount of anthracene also appeared; or possibly, there is a small conversion of the *trans* form to the *cis* during the heating. In the case of 1,5-dichloroanthracene dibromide, the pyrolysis to bromine and 1,5-dichloroanthracene is almost quantitative. Similarly, 1,5-dichloroanthracene dichloride gives large yields of chlorine and 1,5-dichloroanthracene by heating. That this is not quantitative was thought to be due to a partial rearrangement of the *cis* form to the *trans*.

The following reaction [80] takes place at the melting temperature:



Apparently, the original compound melts at 312°, which was shown to be the melting point of the final compound. The melting point of the original compound, taken by the "dip" method, is 165°.

Umbellone dibromide [81] loses hydrogen bromide energetically by distillation at 20 mm. pressure. The products are a hydrocarbon, $C_{10}H_{14}$, an unsaturated bromoketone $C_{10}H_{13}OBr$, and a crystalline dibromo-

[78] von Braun, *Ber.* **60**, 1180 (1927).
[79] Barnett, Cook and Matthews, *Rec. trav. chim.* **44**, 217, 728, 818 (1925).
[80] Kohler and Souther, *J. Am. Chem. Soc.* **44**, 2903 (1922).
[81] Lees, *J. Chem. Soc.* **85**, 641 (1904).

dihydroumbellone, $C_{10}H_{14}OBr_2$, which apparently is formed by the action of hydrogen bromide on the unsaturated bromoketone.

Miscellaneous Halogen Derivatives.

Iodoso-benzene [82] undergoes a disproportionation into phenyl iodide and iodoxy-benzene by heating in boiling water; the yields are practically in accordance with the equation:

$$2C_6H_5IO \longrightarrow C_6H_5I + C_6H_5IO_2.$$

Analogously, iodosopyridines [83] change by heating into iodoxy-pyridines. Diphenyl iodonium iodide, $(C_6H_5)_2I—I$, decomposes [84] quantitatively into phenyl iodide if heated. This change is analogous to the decomposition of quaternary ammonium iodides into alkyl iodide and trialkylamine. Phenyl-iodophenyl iodonium iodide [85] melts at 144° with the formation of equal amounts of phenyl iodide and diiodobenzene.

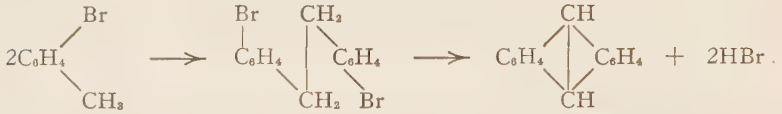
Compounds Containing Halogen Attached to an Aromatic or Heterocyclic Nucleus.

Aryl halides do not decompose as a general rule unless the temperature is very high. This has been mentioned in connection with the pyrogenic decomposition of aromatic hydrocarbons. If aromatic halogen derivatives are maintained at bright red heat [59] for several hours, diphenyl derivatives are formed. Although hydrogen and halogen are eliminated to a certain extent, Meyer and Hofmann never found (unless possibly with the iodides) that two aromatic nuclei became united in the diphenyl derivatives by the carbon atoms that bore the halogens. The fact that tetrabromoanisole boils at about 340° with very little decomposition [86] is ample evidence for their thermostability.

Chlorobenzene gradually decomposes with persistent heating into 4,4′-dichloro-diphenyl, with small amounts of the 2,2′-isomer and also some of 4-chloro-diphenyl. Presumably some of the hydrogen that should have been liberated in this reaction, reacted to produce hydrogen chloride by reducing the C—Cl bond. *p*-Dichlorobenzene is a very stable compound, but by continued heating it yields 2,5,2′,5′-tetrachlorodiphenyl. *p*-Dibromobenzene undergoes the same type of reaction, but in addition to the tetrabromodiphenyl, there may also be isolated the various *o*- and *p*-dibromodiphenyls. Phenyl iodide pyrolyzes into benzene, diphenyl, and a mixture of iododiphenyls. Fluorobenzene yields 4,4′-difluorodiphenyl.

[82] Willgerodt, *Ber.* **26**, 1307 (1893).
[83] Brit. Pat. 259,960, Oct. 17, 1925; *Chem. Abstracts* **21**, 3370 (1927).
[84] Hartmann and Meyer, *Ber.* **27**, 507 (1894).
[85] Hartmann and Meyer, *Ber.* **27**, 427 (1894); Willgerodt and Heusner, *Ber.* **40**, 4077 (1907).
[86] Kohn and Sussman, *Monatsh.* **46**, 575 (1926).

The *o*- or *p*-halogen derivatives of toluene do not undergo the diphenyl type of pyrolysis, but instead the major activity occurs at the methyl side-chain. From *p*-chlorotoluene, Meyer and Hofmann found both the ethane and the ethylene derivatives, $ClC_6H_4CH_2CH_2C_6H_4Cl$ and $ClC_6H_4CH{=}CHC_6H_4Cl$. *p*-Fluorotoluene decomposed rapidly and at a lower temperature into difluorostilbene, $FC_6H_4CH{=}CHC_6H_4F$. *m*-Fluorotoluene gives *symmetrical*-di-*m*-fluorophenyl ethane. As with other iodine compounds, *p*-iodotoluene yields quite a mixture by thermal decomposition; it contains toluene, *symmetrical* diphenylethane, stilbene and *p,p'*-diiodostilbene. It is quite an easy matter to convert *o*-bromotoluene into anthracene; di-*o*-bromophenylethane is considered an intermediate:



In addition, the reaction mixture may contain *o,o'*-dibromostilbene and *o,o'*-dibromodiphenyl.

Tetraiodopyrrole,[87] at 150-200°, forms $(C_4HNI)_n$; at more elevated temperatures it yields $(C_4NH)_n$, a substance which resembles graphite. Tetraiodofuran liberates iodine at 160°, and decomposes at 202° to a black, graphite-like residue. At 450°, tetraiodothiophene loses three atoms of iodine and loses the fourth at red heat. In a vacuum for two or three hours, the three atoms may be removed at 340°, and in a current of carbon dioxide all four are removed at 450°. Hexaiodobenzene decomposes similarly into the "graphite of benzene". Ciusa points out that graphite or $(C_6)_n$ is intimately related to the "graphite of thiophene" $(C_4S)_n$, the "graphite of pyrrole" $(C_4NH)_n$, and the "graphite of furan" $(C_4O)_n$. Tetraiodoimidazole,[88] $\begin{matrix} N{-}CI{=}CI \\ \| \quad\quad | \\ CI{-}\!-\!-\!-NI \end{matrix}$, loses three of the four iodine atoms at 180° and forms the sepia-colored C_3N_2I. The remaining iodine atom is discharged at 420°, giving $(C_3N_2)_n$, which, at red heat, yields cyanogen and carbon.

Inorganic Esters Other Than Alkyl Halides.

Sulfates.

Methods for the preparation of ether and of ethylene which have long been approved consist in the interaction of alcohol and sulfuric

[87] Ciusa, *Gazz. chim. ital.* **52**, II, 130 (1922); **55**, 385 (1926).
[88] Pauly and Waltzinger, *Ber.* **46**, 3129 (1913).

acid. It is unnecessary to isolate ethyl hydrogen sulfate as the intermediate product, but if this is done, it is found that it is stable at 100°, and at more elevated temperatures it decomposes into ethylene and sulfuric acid:[89]

$$C_2H_5—O—SO_3H \longrightarrow C_2H_4 + H_2SO_4.$$

Some sulfurous acid is also formed.

At 220-280°, potassium methyl sulfate[90] decomposes into dimethyl ether and potassium pyrosulfate:

$$2K(CH_3)SO_4 \longrightarrow (CH_3)_2O + K_2S_2O_7.$$

Sodium methyl sulfate pyrolyzes similarly at a slightly lower temperature, but in this case there is 7 percent of a side reaction to yield dimethyl sulfate and sodium sulfate. With lithium methyl sulfate, and with the alkaline-earth (Ca,Ba,Sr) methyl sulfates, the decomposition occurs below 220°, chiefly in the direction of a disproportionation into dimethyl sulfate and the normal sulfate. Very little dimethyl ether is formed. The reactions, therefore, appear to be summed up in the following two equations:

$$(1)\quad 2CH_3MSO_4 \longrightarrow (CH_3)_2SO_4 + M_2SO_4$$

and

$$(2)\quad [(CH_3)_2SO_4 + M_2SO_4] \longrightarrow (CH_3)_2O + M_2S_2O_7$$

Potassium ethyl sulfate,[91] potassium *iso*butyl sulfate, and potassium *iso*amyl sulfate all yield the corresponding olefine and alcohol, and from potassium ethyl sulfate some diethyl ether is produced as well. In each case, sulfurous acid is a product of the reaction. The following data pertain to this study.

TABLE XVIII. *Pyrolysis of Some Potassium Alkyl Sulfates.*

	Weight Grams	Temperature	Olefine	Alcohol	Ether
Potassium ethyl sulfate	73.5	250–350°	ethylene 42.7%	ethanol 3 gm.	diethyl ether 4 cc.
Potassium *iso*butyl sulfate	60	295–330°	butylene 17.4%	isobutyl alcohol 11.7 cc.	.....
Potassium *iso*amyl sulfate	60	240–314°	trimethyl-ethylene 15.3%	isoamyl alcohol 10 cc.	.....

Dimethyl sulfate boils at 188° with but slight decomposition. Its homolog, diethyl sulfate, suffers considerable decomposition by ordinary

[89] Scholvien, *Chem. Zentr.* **1890**, II, 2, 782.
[90] Guyot and Simon, *Compt. rend.* **168**, 1054, 1204 (1919).
[91] Nef, *Ann.* **318**, 40 (1901).

distillation. In fact, diethyl sulfate decomposes very slowly into gaseous products at as low a temperature as 140°. At a constant temperature of 146-150°, 1850 cc. of gas is eventually obtained from 11.7 grams of diethyl sulfate. The following volumes in cubic centimeters are evolved during consecutive 15 minute intervals, 14, 15, 19, 21.6, 26, 33.6, 48, 62, 79, 102. The volume 1850 cc. is 51.76 percent of the calculated amount. In these experiments sulfur dioxide and carbon dioxide, both of which were formed, were intercepted by a wash bottle containing sodium hydroxide solution. The residue in the distilling flask contains 3 grams of sulfuric acid and 1.2 grams of carbon. No carbon monoxide is formed in this reaction.

Di-*n*-propyl sulfate decomposes stormily at 170°, but at 140° the gas evolution is moderate. It gives only 38 percent of the theoretical yield of propylene. From 20 grams of the ester, a residual 3.4 grams of carbon bears testimony to the oxidizing effect of the sulfuric acid. Only 0.7 gram (calculated amount is 10.8 grams) of sulfuric acid appears as a final product. Much the same may be said for the pyrolysis of di-*iso*amyl sulfate. The quantity taken was 13.5 grams; the bath temperature was 190-210° and finally 260°; the yield of trimethylethylene was 40 percent; sulfur dioxide was evolved in quantity. There were only traces of sulfuric acid, and but a small amount of carbon as residue in the flask.

Nitrates.

The vapors of methyl nitrate [92] explode when heated; this might be anticipated because of the proximity of oxidizing and reducing atoms. As might be imagined, investigations in this type of thermal decompositions have not attracted many workers.

The non-catalytic decomposition [93] of purified nitrocellulose at 25° is practically negligible; its period of half-life is 70,000 years. As the substance is purified, the rate of decomposition sinks to a minimum value for a given degree of nitration. Much the same effect is noted in the case of nitroglycerin.[94] Here, the rate of decomposition is a function of the temperature, and between 95-125° it doubles for a rise of 5°. The nitrogen is wholly disengaged as NO_2. This is in contrast to the behavior of guncotton, from which only 40 percent of the nitrogen is evolved as NO_2 at 135°. Nitroglycerin has a higher rate of decomposition than guncotton under similar conditions.

[92] Beilstein, "Handbuch der Organischen Chemie," 4th edition, I, 284.
[93] Farmer, *J. Chem. Soc.* 117, 811 (1920).
[94] Robertson, *J. Chem. Soc.* 95, 1241 (1909).

Hypochlorites.

Comparatively speaking, the tertiary alkyl hypochlorites are stable, but the primary and the secondary alkyl hypochlorites are very unstable. They decompose in the following manner:

$$R{-}CH_2{-}O{-}Cl \longrightarrow RCHO + HCl$$

and

$$R_2CH{-}O{-}Cl \longrightarrow R_2CO + HCl.$$

This type of decomposition is encountered in the preparation of chloral from ethyl alcohol. Ethyl hypochlorite [95] is an intermediate product.

Goldschmidt [96] has demonstrated that ethyl hypochlorite may be preserved in carbon tetrachloride solution at — 15° for 14 hours with only 25 percent decomposition, and still better results at + 20° are claimed by Taylor, McMullin and Gammal. Ethyl hypochlorite decomposes [97] on standing, giving high yields of ethyl acetate, probably by the following steps:

$$C_2H_5OCl \longrightarrow CH_3CHO + HCl,$$

and

$$CH_3CHO + C_2H_5OCl \longrightarrow CH_3{-}CO_2C_2H_5 + HCl.$$

If protected from sunlight, ethyl hypochlorite may be distilled [98] at 36°, but when heated in a sealed tube it decomposes violently.

*Iso*propyl hypochlorite and *iso*butyl hypochlorite [99] show less stability than the normal isomers. Tertiary butyl hypochlorite, however, distils without appreciable decomposition at 79°. If exposed to bright sunlight, or if heated sufficiently, a quiet decomposition ensues which yields methyl chloride and acetone:

$$(CH_3)_3C{-}OCl \longrightarrow (CH_3)_2CO + CH_3Cl.$$

Tertiary amyl hypochlorite is less stable; it boils at 76°, but in so doing it suffers considerable decomposition, presumably in large measure into acetone and ethyl chloride.

Ethyl Perchlorate.

Ethyl perchlorate decomposes [100] if dry even by pouring, but a thin water film stabilizes it sufficiently so that it may be distilled (74°).

Diethyl Sulfite.

Diethyl sulfite,[101] $O{=}S(OC_2H_5)_2$, boils with decomposition at 200° giving sulfur dioxide and diethyl ether.

[95] Chattaway and Backeberg *J. Chem. Soc.* **123**, 2999 (1923).
[96] Goldschmidt, Endres and Dirsch, *Ber.* **58**, 572 (1925).
[97] Taylor, McMullin and Gammal, *J. Am. Chem. Soc.* **47**, 396 (1925).
[98] Sandmeyer, *Ber.* **18**, 1768 (1885).
[99] Chattaway and Backeberg, *loc. cit.;* Backeberg, *J. S. African Chem. Inst.* **8**, 32 (1925). *Chem. Abstracts* **19**, 1850 (1925).
[100] Roscoe, *J. Chem. Soc.* **15**, 213 (1863); *Ann.* **124**, 124 (1862).
[101] Prinz, *Ann.* **223**, 374 (1884).

CHAPTER 7.

ALCOHOLS AND PHENOLS.

Primary Alcohols.

The pioneer work of Berthelot [1] indicated that the simple alcohols, aldehydes and ethers decompose into small quantities of acetylene at red heat. That Berthelot overemphasized the importance of acetylene in such cases has already been mentioned. Very often, acetylene is only found in trivial amounts.

Methanol.

The chief substances formed from the pyrolysis of methanol [2] are formaldehyde, hydrogen and carbon monoxide. A slight decomposition is detectable at 500°, but this does not become rapid until 600°. From 20 grams of methanol, conducted over pumice at 610-630° during one hour, Nef collected 5 cc. of a liquid which seemed to be an aqueous solution of formaldehyde with traces only of methanol. There was no charring, and no olefines appeared to be formed. An analysis of the gases (17.5 liters) gave 61.7 percent hydrogen, 31.7 percent carbon monoxide, 4 percent methane, and 2.6 percent nitrogen. If methanol is maintained [3] for 10 minutes at 650° in a porcelain tube, about one third of it yields a condensable product. The gases of the reactions are: 55.75 percent hydrogen, 33 percent carbon monoxide and 11.25 percent methane. At 1000°, methanol decomposes instantly into the gases: hydrogen, 64.9 percent; carbon monoxide, 33.1 percent; methane, 2 percent; and traces of carbon dioxide. Peytral [4] also studied this decomposition at high temperature by passing the vapors through a platinum tube, 11 cm. × 0.2 cm., at 1150°. Her findings seemed to indicate that the primary effect of heat is dehydrogenation to formaldehyde:

$$CH_3OH \longrightarrow H_2 + HCHO,$$

with a subsequent decomposition of the aldehyde into hydrogen and carbon monoxide. Evidence that these two reactions are not simul-

[1] Berthelot, *Ann. chim. phys.* [3] **33**, 295 (1851); **67**, 52 (1863); *Ann.* **81**, 109 (1852).
[2] Nef, *Ann.* **318**, 191 (1901).
[3] Bone and Davies, *J. Chem. Soc.* **105**, 1691 (1914).
[4] Peytral, *Compt. rend.* **165**, 703 (1917).

taneous is supplied in the CO/HCHO ratio, since this varies with the rate of flow of the methanol. This ratio equals 0.87 when 1.23 mg.-mols are passed per second and it equals 16.75 when half that number are passed. These conclusions are at variance with Bone's postulation that three simultaneous reactions occur, namely, (1) the low temperature dehydration into methylene; (2) the high temperature dehydrogenation into carbon monoxide, perhaps *via* formaldehyde; and (3) the reduction of methylene to methane by the hydrogen of the reaction. One serious criticism of the last mechanism is the fact that ethylene is not observed as a reaction product, and small amounts of this would certainly be anticipated if methylene were an actual intermediate. In other words, it strains the imagination to believe that the methylene is quantitatively reduced to methane, with the total exclusion of any tendency to polymerize.

ETHANOL.

The reaction of dehydrogenation, which is so pronounced with methanol at high temperatures, is also encountered with ethyl alcohol. However, in this case, there is also a simultaneous dehydration into ethylene, and it seems rather obvious that the presence of a hydrogen atom on the neighboring carbon atom is the determining factor for this effect. In Peytral's apparatus,[5] 70 percent of the ethyl alcohol pyrolyzes into acetaldehyde and 30 percent into ethylene. Ipatiew[6] compared the effect of glass tubes and platinum tubes, and noted a very similar type of decomposition in both, the chief difference being that in glass the pyrolysis occurred at a somewhat higher temperature. Through a glass tube at 600°, ethanol[7] gives some evidence of pyrolysis, but none at 500-520°. Ten grams of ethanol, out of 100 grams, decomposes in a glass tube at 610-630° during 70 minutes, forming thereby 0.75 gram of ethylene; 9 grams of acetaldehyde, which in turn breaks down further into about 8 grams of methane and carbon monoxide. About 7 liters of gas results having the following composition: hydrogen, 46.5 percent; methane, 23.4 percent; carbon monoxide, 21.3 percent; and ethylene, 9 percent. In the glass tube at 800-820°, 50 grams out of 140 grams was found to undergo pyrolysis and 9 grams of acetaldehyde was identified. In the platinum tube at 780°, 87 grams out of 117 grams decomposed, and here also, about 9-10 grams of acetaldehyde was isolated. The gaseous products in the two cases were similar, and their composition did not differ materially from that of the 610-630° run.

[5] Peytral, *Bull. soc. chim.* **27**, 34 (1920).
[6] Ipatiew, *Ber.* **34**, 3579 (1901).
[7] Ipatiew, *Ber.* **36**, 1993 (1903); Jahn, *Ber.* **13**, 987 (1880).

Ipatiew estimated that at 800°, about six-sevenths of the alcohol changes into acetaldehyde and hydrogen, and the remaining one-seventh into ethylene and water.

Nef [2] also observed the two simultaneous reactions by which hydrogen and water are eliminated from alcohol by heat, with a preponderance of the former. Seven cc. of distillate was recovered from 30 cc. of absolute ethyl alcohol, passed during 3 hours over pumice at 590-640°. This distillate was 4.75 cc. alcohol and 1.5 cc. water. Acetaldehyde and crotonaldehyde were recognized by their odor. There was formed 12.6 percent of ethylene and 29.4 liters of other gases with the following composition; hydrogen, 35.5 percent; methane, 35.6 percent; and carbon monoxide, 28.9 percent. The fact that nearly molar proportions of these three substances appeared indicated the almost complete secondary decomposition of acetaldehyde.

Senderens [8] mentioned that when alcohol vapors are passed over amorphous carbon, some formaldehyde is produced. Possibly this comes by the catalytic reduction of the carbon monoxide, but apparently this is not Senderens' viewpoint, since he suggests the equation:

$$C_2H_5OH \longrightarrow CH_4 + HCHO.$$

The gases of the reaction are 54.7 percent methane, 35.5 percent ethylene, 4.5 percent carbon monoxide, and 4.8 percent hydrogen. This high percentage of methane and low percentage of hydrogen and carbon monoxide differ materially from the results which have been mentioned.

Müller has recently [9] decomposed alcohol in a novel way. An electric arc from iron and carbon electrodes was played under the surface of 1.1 liters of alcohol in a copper vessel, attached to a copper reflux condenser, for 5 hours. The products of the reaction are given below:

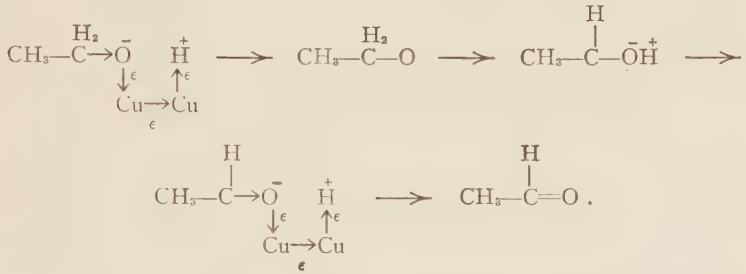
(1) 48 cc. of condensate, boiling point above 12-15°, contains 44 cc. alcohol and 4 cc. of acetaldehyde.
(2) 60 cc. of condensate, collected at —40° to —80°, which in addition to alcohol, contains 8 cc. of acetaldehyde and 2.5 cc. of acetylenes. From the latter may be isolated some butadiyne, $HC{\equiv}C{-}C{\equiv}CH$. About 0.5-1.0 gram of this is formed per liter of alcohol decomposed. It polymerizes above 0°.
(3) 1200 liters of gas from which the 108 cc. of the condensate in (1) and (2) was taken. The remaining gas analyzes as follows: 46.2-49.9 percent hydrogen; 20.4-23.8 percent carbon monoxide; 6.8-20.4 percent paraffins; 6-9.6 percent ethylene; and 7-9.9 percent acetylene.

The Effect of Catalysts.

The two reactions of dehydrogenation and dehydration may be profoundly influenced by catalysts. Adkins and Lazier [10] give an interesting

[8] Senderens, *Compt. rend.* **144**, 381 (1907).
[9] Müller, *Helv. Chim. Acta* **8**, 821 (1925).
[10] Adkins and Lazier, *J. Am. Chem. Soc.* **46**, 2292 (1924).

discussion of this subject. Ethylene may be prepared [11] in excellent yields by passing a mixture of alcohol and steam over kaolin at 400-500°. With an alumina catalyst, also, better yields [12] of ethylene are found if steam is added to the alcohol vapors. Copper or brass catalysts are instrumental in causing a smooth conversion of the alcohol to aldehyde,[13] possibly, as Rideal suggests, because the copper assists in the flow of electrons from O to H. Represented diagrammatically, this becomes:



With *n*-butyl alcohol, a smooth conversion [14] into *n*-butyraldehyde and hydrogen takes place at 220-260° over reduced copper. Similarly, at dull red heat in the presence of brass turnings,[15] *iso*butyraldehyde is formed from *iso*butyl alcohol, and trimethyl-acetaldehyde, in 52 percent yields, from tertiary butyl carbinol. The latter reaction permits the isolation of 70 percent of the theoretical amount of hydrogen.

Doyarenko [16] has studied the effect of alumina in promoting the dehydration of cyclopropyl carbinol, and of methyl cyclopropyl carbinol. The dehydration becomes more nearly complete with an increase in temperature, and reaches its maximum at 350-400°, where the amount of water liberated approaches the theoretical and the yield of the volatile hydrocarbon is the greatest.

Francis has calculated [17] the free energies of some alcohols, and proposes for the dehydration reaction:

$$C_nH_{2n+2}OH \longrightarrow C_nH_{2n} + H_2O,$$

the following equation as an approximation to the truth:

$$\Delta F \text{ (free energy)} = 15{,}110 - 1410n - 25.6T.$$

[11] Brooks, *Chem. Met. Eng.* **22**, 629 (1920).
[12] Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co., **1922**, paragraph 180 h, by W. D. Bancroft.
[13] Rideal, *Inst. Intern. Chim. Solvay*, 2ième Cons. Chim. **1926**, 480.
[14] Sabatier and Senderens, *Compt. rend.* **136**, 923 (1903).
[15] Franke and Groeger, *Monatsh.* **43**, 55 (1923); Franke and Hinterberger, *ibid.* **43**, 655 (1923); Danilov, *Chem. Abstracts* **22**, 2138 (1928).
[16] Doyarenko, *Ber.* **60**, 1536 (1927).
[17] Francis, *Ind. Eng. Chem.* **20**, 283 (1928).

From this, for the dehydration of ethanol, the free energy would become zero at about 207° C. In this connection, therefore, it is interesting to observe that actual catalytic operations [18] are carried out at higher temperatures, 250-400° C.

n-Propyl Alcohol.

If *n*-propyl alcohol [2] is passed over pumice at 595-620° at a rate of 70.8 grams in 105 minutes, 47 grams of distillate is formed which is largely propanol (25 grams), but which also contains water (17 grams) and 4 cc. of propionaldehyde. The dibromides, 20.5 grams with a boiling point of 130-135° and 12.4 grams with a boiling point of 135-141°, which result by passing the gases through bromine water are obviously a mixture of ethylene and propylene bromides. Nearly 19 liters of permanent gas accrue in this reaction, which contain by volume, 41.22 percent hydrogen, 26.88 percent methane, 22.45 percent carbon monoxide and 9.45 percent ethane. Comparable results are obtained at a much higher temperature [19] if a much shorter tube (11 cm. platinum) is employed with a more rapid rate of flow (1.3 grams per min.). The following data are from the work of Peytral:

Table XIX. *Pyrolysis of Propanol.*

	I	II	III	IV
Time (seconds)	34	88	59.5	65
Grams of propanol	0.832	3.210	3.108	3.611
Rate of flow (mg./sec.)	24	36	52	55
Volume of gases (cc.)	561	586	554	576

Table XX. *Analysis of Gases from Pyrolysis of Propanol.*

	Percent			
Propylene	18.8	30.3	36.7	37.8
Ethylene	8.5	4.4	0.6	0.7
Acetylene	2.3	0.6	0.6	0.5
Carbon monoxide	21.5	17.1	13.6	13.1
Hydrogen	38.2	35.5	36.1	36.0
Ethane	10.7	12.1	12.4	11.9

Three equations are postulated to interpret these results; the first two are the customary reactions of dehydration and dehydrogenation:

$$CH_3CH_2CH_2OH \longrightarrow H_2 + CH_3CH_2CHO$$

$$CH_3CH_2CH_2OH \longrightarrow H_2O + CH_3CH{=}CH_2.$$

The third is a decomposition into formaldehyde and ethane; traces of formaldehyde were actually identified:

$$CH_3CH_2CH_2OH \longrightarrow HCHO + CH_3{-}CH_3.$$

[18] Moser and Lindinger, *Monatsch.* **44**, 141 (1923); Hisamura and Imaoka, *Kwaken Hôkohu* No. 7, 1 (1923); *Chem. Abstracts* **18**, 813 (1924); Kesting, *Z. angew. Chem.* **38**, 362 (1925).
[19] Peytral, *Bull. soc. chim.* **35**, 960 (1924).

In the first reaction the aldehyde pyrolyzes further into carbon monoxide and ethane, and the ethane from this source or from the third reaction is further transformed in part into ethylene and acetylene, the amounts diminishing with an increased rate of flow. The acetylene comprises but 0.004 of the gaseous volume. Curiously enough, methane was not reported in this work. Most probably the third reaction is rather insignificant, but it is interesting to note that a similar reaction was already mentioned with ethanol when a carbon catalyst was used, and it will be encountered later with such alcohols as acetol, CH_3—CO—CH_2OH. Furthermore, it becomes the exclusive reaction in the heating of compounds with the grouping $>N—CH_2OH$. These cases, however, are hardly comparable to propanol.

Butyl Alcohol.

The effect of moderate heating of *n-butyl alcohol* has not been studied except with catalysts present, but it has been found that at 750° most of it is converted into gaseous products when the rate of decomposition [20] is 70 grams in 4 hours. Only about 5 grams of condensed liquid is obtainable. Some butadiene is present in the latter (0.8 gram of the tetrabromide), but more of it is present in the gaseous products (1.2 grams of the tetrabromide). The gaseous products contain fairly large amounts of ethylene and propylene, as witnessed by the fact that 47.5 grams of dibromides, boiling between 130-138°, are obtainable.

Isobutyl Alcohol.

With isobutyl alcohol, the two reactions leading to *iso*butyraldehyde and *iso*butylene, respectively, are both encountered at 600-620°, but there are various side reactions which come into play. If pumice is placed in the reaction tube, the evidence seems to indicate that the greater tendency is for dehydrogenation rather than dehydration. As was pointed out this reaction may be accelerated by the presence of copper or brass turnings, or it may be almost entirely inhibited in the presence of dehydrating catalysts,[21] such as phosphorus pentoxide on pumice, alumina, or aluminum phosphate. Thus, even at 430-480°, *iso*butyl alcohol gives a quantitative yield of butylenes (72 percent *iso*- and 28 percent β) when passed over phosphorus pentoxide. An analysis of Nef's data reveals the following interesting molar relationships. If 0.89 mol (65.9 grams) of *iso*butyl alcohol are passed over pumice at

[20] Staudinger, Endle and Herold, *Ber.* **46**, 2477 (1913).
[21] Nef, *Ann.* **318**, 27, 208 (1901).

620° during three hours, there are formed at least 0.16 mol of butylene, 0.13 mol of ethylene and 0.04 mol of propylene, and in addition 32 liters (1.4 mols) of other gases. Nef's method of analysis was to polymerize butylene by sulfuric acid wash bottles, which process would also partially convert propylene into propyl hydrogen sulfate; the remaining propylene, and the total quantity of ethylene was then converted into dibromides. If the experiment is repeated at a slower rate of speed, it is found that 22 grams out of the original 65.6 grams may be recovered, if the elapsed time is 75 minutes. Thus, for 0.59 mol which are actually decomposed, the data indicate that 0.30 mol of hydrogen are formed; also, 0.19 mol of methane, 0.186 mol of carbon monoxide; about 0.1 mol of an aldehyde mixture, chiefly *iso*butyraldehyde with some propionaldehyde; 0.12-0.13 mol of ethylene (mixed with some propylene); 0.11-0.12 mol of butylene (mixed with some propylene); and 0.06 mol of ethane. It is interesting to note that the number of mols of hydrogen is nearly equalled by the sum of the mols of aldehyde and its decomposition product, carbon monoxide. This should be the case. Also, it may be pointed out that this value exceeds the number of mols of butylene, which is the major product by the simultaneous reaction of dehydration.

None of these reactions have indicated that carbon dioxide may be a product of thermal decomposition of alcohols. That the quantity of carbon dioxide formed is largely dependent on catalysts may very well be true. Lazier and Adkins [22] suggest a novel explanation for its presence, and disfavor the thought that it may come from carbon monoxide by disproportionation or by reaction with water. Furthermore, they disfavor the thought that the carbon dioxide comes by decarboxylation of an ester which may be formed by a condensation of two aldehyde molecules. In brief, their explanation postulates an ephemeral existence of ketenes, which might react with the aldehydes to give olefines and carbon dioxide. Thus, the mechanism postulated is alcohols to aldehydes and hydrogen, and then to ketenes and two mols of hydrogen, following which there is the reaction:

$$R_2C{=}CO + OCHR' \longrightarrow R_2C{=}CHR' + CO_2.$$

They suggest that the reason for the non-observance of ketenes is because of their reaction in this manner, or of their reaction with water to yield acids, or with hydrogen to regenerate the aldehyde. Obviously, there is much in this which is speculative, but at least it is stimulating.

[22] Lazier and Adkins, *J. Phys. Chem.* **30**, 895 (1926).

Isoamyl Alcohol.

In spite of the fact that several workers have studied the problem of pyrolysis of *iso*amyl alcohol, it must be admitted that the problem is not yet completely solved. For example, amylene appears to be a product of the reaction at 550° if 1.8 mols are passing per hour, but at one-third this rate and at 600° this does not appear to be the case. Furthermore, no satisfactory method of analyzing a mixture of ethylene, propylene, butylene, butadiene, and amylene has been developed and this is the mixture which is encountered from this reaction.

A copper tube is not appreciably catalytic,[23] and in a copper tube filled with silica, Ipatiew demonstrated that a mixture of amylenes was formed at 540°. Trimethyl ethylene was always prominent in the amylene mixture. Most of Ipatiew's work of a similar nature was performed in the presence of an alumina catalyst. Norris and Reuter [24] performed similar experiments with *iso*amyl alcohol, which was stated to contain about 10 percent of active amyl alcohol; in their work, a silica tube, both with and without catalysts, was used. When catalysts were not employed, at 515°, about one-third of the alcohol decomposed into water and *iso*propylethylene, and about one-third of the latter rearranged into trimethylethylene. To obtain these results, the alcohol was passed at a rate of 1.67 mols per hour and it was found that half of the alcohol was unchanged and that very little permanent gas was formed. At 555°, these reactions become complicated by the fact that a considerable portion of the pentene is cracked into gaseous products, even though a somewhat faster rate of flow is maintained. It is rather interesting to note that the thin coating of carbon which deposits on the silica tube appears to cut down immensely the rate of decomposition of the alcohol. If it is desired to prepare *iso*propylethylene from *iso*amyl alcohol by catalytic dehydration by heat, alumina should be used as the catalyst and the temperature should be near 450°. If it is desired to get the largest yield of trimethylethylene by the reaction, aluminum sulfate at 345° appears to be the best catalyst of those studied.

With regard to the lower olefines formed by the pyrogenic decomposition of *iso*amyl alcohol, Nef's data [21] are the most detailed. At a temperature of 580-620°, 100 grams of the alcohol gives 12.5 grams of butylene (identified as the polymer), 22 liters of non-olefinic gases, and 47 grams of the dibromides of ethylene, propylene and butylene; 34.6 grams of the latter boiled at 133-140°, and 6.6 grams at 140-150°. Amylene was stated to be absent. Another experiment, using 56.8 grams of

[23] Ipatiew, *Ber.* **36**, 1991, 2000 (1903).
[24] Norris and Reuter, *J. Am. Chem. Soc.* **49**, 2637 (1927).

*iso*amyl alcohol (0.64 mol), was studied more completely. The elapsed time was 65 minutes; therefore, the rate of flow was 0.6 mol per hour. One-fifth of the alcohol was recovered, besides the 14.3 grams of other liquid products of the reaction from which were isolated water, valeraldehyde, acetaldehyde and a ketone, boiling point (12 mm.) 85-90°. Over 60 grams of a mixture of ethylene, propylene and butylene bromides was collected in the bromine wash bottle, and also 7 grams of tribromobutane, and 0.7 gram of butadiene-tetrabromide. Caventou was the first to recognize butadiene [25] as one of the products of this thermal decomposition. Of the 15.9 liters of gas that Nef collected, the analysis shows the composition to have been 39 percent methane, 28.6 percent hydrogen, 23.85 percent carbon monoxide and 8.55 percent ethane. Thus, from 0.52 mol of unrecovered *iso*amyl alcohol, there are formed 0.28 mol of methane, 0.20 mol of hydrogen, 0.17 mol of carbon monoxide and 0.06 mol of ethane. It is difficult to estimate the exact composition of the olefines from the available data.

As would be expected, the yield [26] of butadiene is greater at 750° than at the lower temperatures, although the yield in both cases is trivial. Isoprene is not formed. From 50 grams of *iso*amyl alcohol, there were isolated 42 grams of a mixture of ethylene and propylene dibromides, and 2.5 grams of butadiene tetrabromide. Considerable water, but no tars, were condensed from the vapors.

Benzyl Alcohol.

None of the simple aliphatic alcohols that have been considered give any evidence that the ethers are products of the reactions. Whenever dehydration has occurred, olefines or the decomposition products of olefines are the resultant products. With benzyl alcohol, however, the ether is a product of reaction by heat alone. Thus, if 30 grams of benzyl alcohol [27] (boiling point 207°) is maintained at 210-215° for 5 days, 6 grams of the alcohol is recoverable, and in addition there are 2 grams of water, 3 grams of dibenzyl ether, and 17 grams of decomposition products of the latter, chiefly toluene and benzaldehyde. This reaction will be of assistance in the interpretation of the pyrolysis of mandelic acid and of benzaldehyde. (See under dibenzyl ether, for its pyrolysis.)

$$2C_6H_5—CH_2OH \longrightarrow C_6H_5CH_2—O—CH_2C_6H_5 + H_2O$$

α-Naphthyl carbinol, $C_{10}H_7—CH_2OH$, behaves similarly,[28] and distils with partial decomposition into the ether and water.

[25] Caventou, *Compt. rend.* **56**, 646, 712 (1863); *Ann.* **127**, 93 (1862).
[26] Staudinger, Endle and Herold, *Ber.* **46**, 2467 (1913); Thiele, *Ann.* **308**, 339 (1899).
[27] Lachman, *J. Am. Chem. Soc.* **45**, 2358 (1923).
[28] Pommereau, *Compt. rend.* **172**, 1503 (1921).

Allyl Alcohol.

Allyl alcohol is related structurally to benzyl alcohol, but it has never been shown to undergo thermal decomposition into diallyl ether. It appears to behave like other aliphatic alcohols and to undergo [29] two first-order reactions:

$$\mathrm{CH_2{=}CH{-}CH_2OH} \begin{cases} \nearrow \mathrm{H_2} \\ \searrow \mathrm{H_2O} \end{cases} \begin{array}{l} + \ \mathrm{CH_2{=}CH{-}CHO} \longrightarrow \mathrm{H_2} + \mathrm{C_2H_4} + \mathrm{CO} \\ + \ [\mathrm{CH_2{=}C{=}CH_2}], \end{array}$$

and

$$[\mathrm{CH_2{=}C{=}CH_2}] + 2\mathrm{H} \longrightarrow \mathrm{CH_3{-}CH{=}CH_2}.$$

Allene apparently was not isolated as such, but it is interesting to note that Mlle. Peytral considered it essential in the mechanism. The dehydrogenation reaction [30] is twice as prominent as the one of dehydration.

Other Primary Alcohols.

In the cases to follow, there is more than one functional group, and this is largely responsible for the course of the reactions. If ring formation is possible, it is frequently the major reaction.

Methyl β-hydroxyethyl-carbamate [31] changes into μ-oxazolidone by distillation:

$$\mathrm{HOCH_2CH_2NH{-}CO{-}OCH_3} \longrightarrow \mathrm{CH_3OH} + \begin{array}{l} \mathrm{CH_2{-}\!-\!-CH_2} \\ \quad | \qquad\quad | \\ \mathrm{O{-}CO{-}NH} \end{array}$$

The amide,[32] $\mathrm{HOCH_2CH_2NHCONH_2}$, behaves similarly on distillation.

o-Benzeneazo-benzyl alcohol,[33] $\mathrm{HOCH_2{-}C_6H_4{-}N{=}N{-}C_6H_5}$, gives small yields of *o,o'*-azodiphenylmethane, $\mathrm{C_6H_4{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{N{=}N}\end{smallmatrix}{>}C_6H_4}$, at 130°, but considerably more of 2-phenyl indazole, $\mathrm{C_6H_4{<}\begin{smallmatrix}\mathrm{CH}\\ \mathrm{N}\end{smallmatrix}{>}N{-}C_6H_5}$. The latter compound may be prepared more smoothly at 80° with sulfuric acid (50 percent). Water is eliminated from *o-iso*propylamino-benzyl alcohol [34] by distillation, as 2,2-dimethyl indoline is formed:

$$\mathrm{C_6H_4{<}\begin{smallmatrix}\mathrm{CH_2OH}\\ \mathrm{NH{-}CH(CH_3)_2}\end{smallmatrix}} \longrightarrow \mathrm{C_6H_4{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{NH}\end{smallmatrix}{>}C(CH_3)_2} + \mathrm{H_2O}.$$

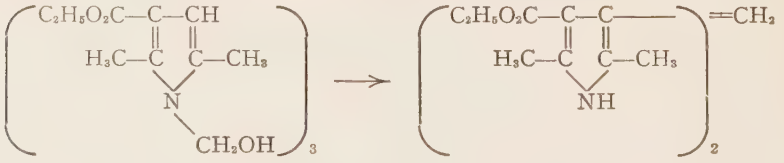
[29] Peytral, *Bull. soc. chim.* **29**, 39 (1921).
[30] For the preparation of divinyl from buten-2-ol-1 at 400° and 60 mm. over kaolin, *see* Kyriakides, *J. Am. Chem. Soc.* **36**, 986 (1914).
[31] Franchimont and Lublin, *Rec. trav. chim.* **21**, 45 (1902).
[32] Knorr and Roessler, *Ber.* **36**, 1281 (1903).
[33] Freundler, *Compt. rend.* **136**, 1137 (1903); **138**, 1276 (1904).
[34] Paal and Laudenheimer, *Ber.* **25**, 2974 (1892).

2-Dimethylamino-5-methyl-benzyl alcohol [35] follows a different course, when heated at 180° with zinc chloride, giving a derivative of indole (not indoline). *o*-Nitrosobenzyl alcohol becomes dehydrated [36] in hot water, forming anthranil, $C_6H_4<\begin{matrix}CH\\|\\N\end{matrix}>O$.

Benzoyl carbinol, $C_6H_5COCH_2OH$, cannot be distilled [37] at ordinary pressure without decomposition. Formaldehyde is evolved and benzaldehyde is the product of distillation. Acetol,[38] CH_3COCH_2OH, seems to break up in a similar manner by heating to give formaldehyde and acetaldehyde. (Compare the behavior of α-ketonic acids.) Another functional group which gives formaldehyde by heating is the $N—CH_2OH$ group. There seem to be no exceptions among the compounds that have been investigated. *N*-Methylol benzamide [39] melts at 104-106°, and decomposes a few degrees higher into benzamide and formaldehyde:

$$C_6H_5CONH—CH_2OH \longrightarrow C_6H_5CONH_2 + HCHO.$$

Similarly, *N*-methylol propionamide [40] changes into formaldehyde and propionamide; *N*-methylol phthalimide [41] into phthalimide; and *N*-methylol-methylene-dibenzamide,[39] $C_6H_5CONHCH_2—N(CH_2OH)—COC_6H_5$, above its melting point, 182°, into methylene dibenzamide. It has recently been shown [42] that when tris-(1-hydroxymethyl-2,5-dimethyl-3-carbethoxypyrrole) is heated at 180°, large amounts of formaldehyde are evolved, and bis-(2,5-dimethyl-3-carbethoxypyrryl-4)-methane remains.



Secondary Alcohols.

Isopropyl Alcohol.

Nef studied the pyrolysis [43] of *iso*propyl alcohol at 615-620° over pumice, and the mode of procedure was similar to that with the primary alcohols. Forty grams of the alcohol per hour gives 20.8 grams of dis-

[35] von Braun and Kruber, *Ber.* **45**, 2985 (1912).
[36] Bamberger, *Ber.* **36**, 839 (1903).
[37] Hunaeus and Zincke, *Ber.* **10**, 1487 (1877).
[38] Nef, *Ann.* **335**, 209, 250 (1904).
[39] Einhorn, *Ann.* **343**, 224 (1905).
[40] Einhorn, *Ann.* **361**, 113 (1908).
[41] Sachs, *Ber.* **31**, 1231 (1898).
[42] Fischer and Nenitzescu, *Ann.* **433**, 113 (1925).
[43] Nef, *Ann.* **318**, 206 (1901).

tillate, 51 grams of crude olefine bromides and 9 liters of fixed gases. The distillate contains acetone (8.8 cc.), water and unchanged *iso*propyl alcohol. Fractionation of the bromides gives 37 grams of propylene bromide, boiling point 135-140°, and 7 grams of butylene bromide, boiling point 140-146°, and 0.15 gram of butadiene tetrabromide. As would be expected, therefore, the chief unsaturated hydrocarbon of the reaction is propylene. The gases, by volume, are 60.7 percent hydrogen, 31.3 percent methane quite free from other paraffins, and 8 percent carbon monoxide. A precipitate of aldehyde resin (acetaldehyde) may be demonstrated by an alkaline wash bottle, and in these original gases from the furnace there is about 1 percent by volume of carbon dioxide.

These results provide a basis for speculation regarding the probable reaction mechanism. First of all, there is dehydration into propylene. From 0.66 mol of *iso*propyl alcohol there is formed 0.18 mol of propylene and an undetermined amount of water. Since methane is the only gaseous paraffin, this indicates the inertness of hydrogen towards propylene at 620°. Secondly, there is dehydrogenation into acetone. The data indicate 0.24 mol of hydrogen and 0.13 mol of acetone. This discrepancy in the amounts of acetone and hydrogen is accounted for by the fact that some acetone was probably lost, whereas none of the hydrogen should have been. The method of collection is nearly quantitative for hydrogen but not so for acetone. Furthermore, some of the acetone may have suffered further pyrolysis (into ketene and methane), and some of the hydrogen may have been formed by secondary reactions and not exclusively from the reaction under discussion. In the third place, the production of methane and of acetaldehyde or carbon monoxide indicates a scission into methane and the aldehyde. The quantity of acetaldehyde was not estimated, but 0.12 mol of methane and 0.03 mol of carbon monoxide indicate a possible 0.09 mol each of methane and acetaldehyde which were formed by the primary reaction, and 0.03 mol each of methane and carbon monoxide by the subsequent pyrolysis of acetaldehyde. However, it is possible that some of the methane of this reaction comes from other sources, such as the pyrolysis of acetone, and it is also possible that the aldehyde may come from the reduction of ketene. If 0.18 mol of *iso*propyl alcohol decomposed by the first reaction, 0.24 by the second, and 0.09 by the third, there is still a difference of 0.15 mol from the original 0.66. Possibly that is the amount which Nef recovered.

Other work (non-catalytic) on simple secondary alcohols seems not to have been done. Hydroxy-acids such as lactic or mandelic, or

hydroxy-ketones which are also secondary alcohols will be discussed in a later chapter.

Alkyl Aryl Carbinols.

Ethyl *p*-anisyl carbinol is easily dehydrated [44] by heat; even by vacuum distillation (140° at 15 mm.), there is a partial conversion into anethole, $CH_3OC_6H_4CH{=}CHCH_3$. The corresponding *p*-dimethylamino compounds [45] $(CH_3)_2NC_6H_4CHOH{-}CH_2CH_3$ and $(CH_3)_2NC_6H_4CHOH{-}CH_2C_6H_5$ are readily dehydrated to the unsaturated compounds merely by distilling them in a vacuum. The lower homolog, namely, methyl *p*-dimethylaminophenyl carbinol, is not successfully converted into an unsaturated derivative by this method.

Aromatic Secondary Alcohols.

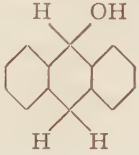
Of the secondary alcohols which are exclusively aromatic, *benzohydrol* is the simplest, and it has been the most extensively studied. As with the more elementary compounds, the processes of dehydration and of dehydrogenation both occur, the former leading to dibenzohydryl ether or its decomposition products and the latter to benzophenone. Linnemann [46] first noticed the ether, $((C_6H_5)_2CH)_2O$, during the distillation of benzohydrol (300°), and Nef confirmed this. He observed that 32 grams of the ether could thus be obtained [47] from 46 grams of diphenyl carbinol, but he advised against this method as a practical means of preparation because of its troublesome features. As will be shown later, this is due in part to the instability of the ether at this temperature of formation. It is interesting to note that pure benzohydrol may be distilled at atmospheric pressure without decomposition, but that it decomposes very readily if only traces of hydrogen chloride [48] are present. From 20 grams of benzohydrol (Nef), refluxed for 3 or 8 hours, there are formed 7.5 grams of tetraphenyl-ethane, 6.1 grams of benzophenone isolated as the phenylhydrazone, and 2.5 grams of diphenyl methane. In spite of the absence of tetraphenyl-ethylene, Nef maintained that the primary dissociation was elimination of water, giving diphenyl methylene. This bivalent compound was then considered to be the active agent in the formation of the compounds actually isolated. These results are practically identical to the results from the ether under similar treatment.

[44] Hill and Hofmann, *Ber.* **37**, 4188 (1904).
[45] Sachs and Sachs, *Ber.* **38**, 511 (1905).
[46] Linnemann, *Ann.* **133**, 9, 14 (1865).
[47] Nef, *Ann.* **298**, 235 (1897).
[48] Sabatier and Murat, *Compt. rend.* **158**, 534 (1914).

No reference was made by Nef to an actual hydrogen evolution, but Knoevenagel and Heckel [49] showed that one-fourth of a mol of it was liberated at 300° in two hours. In this connection, one of Nef's experiments becomes interesting. Ten grams of benzohydrol was refluxed at 300° in a stream of carbon dioxide for 7.5 or 12 hours. Except for the stream of carbon dioxide, the conditions seem the same as in his other experiment, yet there was no trace of tetraphenyl-ethane, and 4.5 grams of the ether was formed. As before, there was diphenylmethane (1.2 grams) and about the same amount of benzophenone (2 grams of the phenylhydrazone). The obvious suggestion is that hydrogen was removed more rapidly in this case.

Phenyl *o*-tolyl carbinol [50] decomposes on distillation, presumably into phenyl-*o*-tolyl-methane and phenyl *o*-tolyl ketone. With 9-hydroxyfluorene, ether formation is apparent by long heating [51] above its melting point, 153°:

$$2(C_6H_4)_2CHOH \longrightarrow H_2O + ((C_6H_4)_2CH)_2O.$$

It has recently been reported [52] that dibiphenylyl carbinol, melting point 106°, gradually solidifies to an isomeric form, having a melting point of 151°. When dihydroanthranol,[53] 

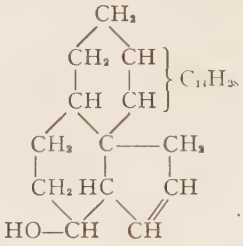
, is warmed with water or alcohol, anthracene forms readily.

The structure of *cholesterol* has not been completely elucidated, but it is definitely known that it is a secondary alcohol. Water is eliminated and cholesteryl ether is formed [54] when it is heated for three hours at 200° with fuller's earth. Hydrocarbons, such as cholesterylene, are produced on heating at 280° for 7 hours. Since cholesterol is an optically active natural product, it is regarded by these authors as the precursor of natural petroleum. In this connection, therefore, it is interesting [55] to indicate that Zelinskii has prepared a distillate almost identical with crude petroleum, by heating 20 gram portions of cholesterol with 4 grams of aluminum chloride over a free flame.

If cholesterol vapors [56] are passed over a heated platinum wire (250° and 11 mm.), the products of the reaction contain about 10 percent of

[49] Knoevenagel and Heckel, *Ber.* **36**, 2817 (1903).
[50] Chichibabin, *J. Russ. Phys. Chem. Soc.* **41**, 116 (1910); *Chem. Abstracts* **4**, 1488 (1910).
[51] Barbier, *Compt. rend.* **80**, 1396 (1875).
[52] Straus and Demus, *Ber.* **59**, 2426 (1926).
[53] von Perger, *J. prakt. Chem.* [2] **23**, 146 (1881).
[54] Steinkopf and others, *J. prakt. Chem.* **100**, 65 (1919).
[55] Zelinskii, *Ber.* **60**, 1793 (1927).
[56] Fischer and Treibs, *Ann.* **446**, 241 (1925).

naphthalene, a small amount of styrene, and the hydrocarbons $C_{15}H_{12}$, $C_{18}H_{14}$ and $C_{14}H_{10}$. The gaseous products are 5 percent hydrogen, 30 percent unsaturated hydrocarbons, and 65 percent saturated hydrocarbons. No more than traces of acetylene are formed. Windaus [57] has done most to elucidate the structure of cholesterol, and the formula he favors is



To form cholesterylene, water is eliminated, presumably with hydroxyl and an adjacent hydrogen.

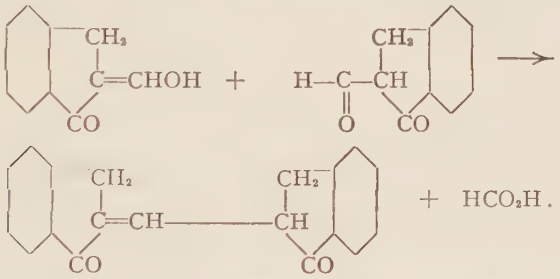
The dry distillation of cholesterol [57a] at atmospheric pressure gives not only water, hydrogen and a complex mixture of low-boiling hydrocarbons, but also cholestenone and ψ-cholestene. It is considered that the cholestenone arises from a dehydrogenation reaction of the cholesterol, and that the hydrogen so formed changes cholesterylene (the immediate dehydration product of cholesterol) into ψ-cholestene. By distillation of cholesterol with activated charcoal,[57b] an oil is formed which contains chrysene and also some hydrochrysene.

Enols.

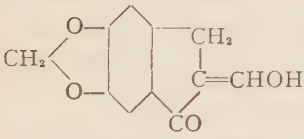
The grouping, C=CH—OH, is known to be extremely unstable unless it is stabilized [58] by a carbonyl group. The literature on keto-enol tautomerism is too vast to be included in such a work as this, but a few cases may be cited to show the effect of heat. Vinyl alcohol or *iso*acetone are both unknown. Attempts to prepare them always give, instead, acetaldehyde and acetone. Triphenyl-vinyl alcohol is referred to frequently in the literature as being a stable compound, but in view of recent work [59] with the related compound, $(C_6H_4)_2C{=}C(OH){-}C_6H_5$, diphenylene-phenyl-vinyl alcohol, there is reason to doubt this. Phenyl-diphenylenevinyl alcohol is isolable in the form of yellowish-white

[57] Windaus, Rosenbach and Riemann, *Z. physiol. Chem.* **130**, 113 (1923).
[57a] Heilbron and Sexton, *J. Chem. Soc.* **1928**, p. 347.
[57b] Tsukamoto, *J. Pharm. Soc. Japan* **48**, 123 (1928); *Chem. Abstracts* **22**, 2361 (1928).
[58] *See* Erlenmeyer, *Ber.* **13**, 309 (1880); Erlenmeyer, Jr., *Ann.* **316**, 75 (1901).
[59] Meyer and Gottlieb-Billroth, *Ber.* **54**, 575 (1921).

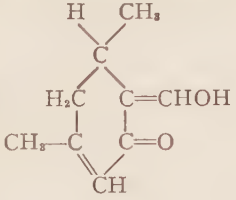
crystals which very quickly undergo isomerization into the keto-isomer, 9-benzoyl-fluorene, which is colorless. Forty-five percent of the solid enol form is converted into the ketone in 4 hours, and 97 percent in 6 hours. As is well known, ethyl acetoacetate and related compounds may be isolated in the enol form, and this is due to the —CO—CH_2—CO— arrangement of atoms. Similarly, it is interesting to note[60] that C_6H_5CO—CH=CHOH is more stable than C_6H_5CO—CH_2—CHO. Hydroxymethylene camphor and related compounds are stable at fairly high temperatures. They may be distilled in a vacuum or in steam. However, 2-hydroxymethylene-1-hydrindone[61] is quite markedly unstable, undergoing, at 130°, a remarkable condensation that involves the loss of one mol of formic acid from two of the substances. The yields of both products are good. Possibly, as Ruhemann and Levy suggest, there is a partial transformation of the enol into the keto form, and then an interaction of these two isomers:



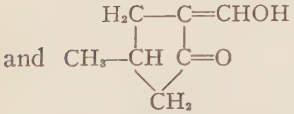
A similar change occurs with the methylenedioxy derivative,



, but at a higher temperature, 160-170°. Other hydroxymethylene compounds prepared by these investigators did not change in this manner. Thus,



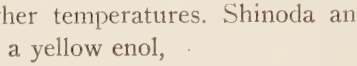
and



, an oil and a solid, may be distilled in a

[60] Claisen, *Ber.* **25**, 1781 (1892).
[61] Ruhemann and Levy, *J. Chem. Soc.* **101**, 2543 (1912).

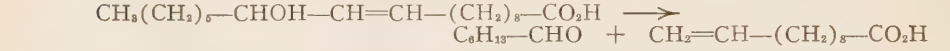
vacuum without change at temperatures of 125° and 77° respectively and at pressures of 15-12 mm. There is no evidence, however, of the effect of higher temperatures. Shinoda and Sato [62] record the transformation of a yellow enol,



into the colorless keto isomer under the influence of heat.

Castor Oil.

Castor oil contains unsaturation of the allyl alcohol type, but the alcoholic hydroxyl is on a secondary carbon atom rather than a primary. About 50 years ago, it was discovered [63] that it changes by vacuum distillation into heptaldehyde (18 percent yield) and undecylenic acid (10 percent yield). Since ricinoleic acid is in the volatile portion, it may be considered to be an intermediate product. The equation, therefore, is:



Krafft's method for the preparation of undecylenic acid, while satisfactory for small quantities, is stated [64] to be unsatisfactory for large amounts. The correctness of the structure [65] of this acid is beyond question as has been recently shown by Noller and Adams. In Krafft's experiments, the volatile portion represents about one-third to one-half the volume of the original castor oil. This distillate is half heptaldehyde, which may be readily purified. The residue in the retort is a spongy, saponifiable mass. This type of scission of an alcohol into two smaller organic molecules is more frequently encountered in tertiary alcohols.

Aldol.

Two general reactions are encountered in the pyrolysis of aldol. It changes into crotonaldehyde [66] at about 165° or lower, and this may be prepared in the laboratory by slow distillation through a column. A recent patent recommends the use of nitrogen as an inert diluent. The importance of crotonaldehyde is growing at the present time. It may be hydrogenated to butyraldehyde or to *n*-butyl alcohol. Aldol cannot be distilled in a vacuum (80° at 20 mm.) without some decomposition into

[62] Shinoda and Sato, *J. Pharm. Soc. Japan* No. **548**, 850 (1927); *Chem. Abstracts* **22**, 767 (1928).
[63] Krafft, *Ber.* **10**, 2034 (1877); Becker, *Ber.* **11**, 1412 (1878).
[64] Bagard, *Bull. soc. chim.* [4] 1, 346 (1907).
[65] Noller and Adams, *J. Am. Chem. Soc.* **48**, 1075 (1926).
[66] Wurtz, *Compt. rend.* **87**, 45 (1878); **97**, 1525 (1883). Carbide and Carbon Chemicals Corporation, Brit. Pat. 242,521, Mar. 31, 1925; *Chem. Abstracts* **20**, 3696 (1926). Hartung and Adkins, *J. Am. Chem. Soc.* **49**, 2521 (1927).

acetaldehyde, a reaction which involves scission of the carbon chain, and which is the reversal of its method of formation. The major reaction is the former, and Grignard and Reif [67] have given directions for the preparation of crotonaldehyde by heating aldol in a flask at 85°, but this process is a tedious one.

Aldol polymerizes [68] on standing into paraldol, $(C_4H_8O_2)_2$. Heat is evolved in this process. If aldol is maintained for 4-6 hours in a sealed tube [69] at 160-170°, the product is homogeneous, and slightly colored. Only a small amount of crotonaldehyde is isolable by distillation, but a 15 percent yield, and in some cases more, of an isomer of aldol, boiling point (15 mm.) 170°, is formed. This substance may also be formed by heating paraldol similarly. Another substance, "isodialdan", $C_{16}H_{28}O_6$, is reported [70] to be formed in small yields by heating aldol at 125°, followed by vacuum distillation.

Propionaldol,[71] formed from propionaldehyde in the presence of sodium acetate, boils at 95° at a pressure of 23 mm. With ordinary distillation it reverts in part to the original aldehyde, but chiefly it gives methyl ethyl acrolein:

$$CH_3CH_2CHOH—CH(CH_3)CHO \longrightarrow H_2O + CH_3CH_2CH{=}C(CH_3)CHO.$$

The aldol from *n*-butyraldehyde, $C_3H_7—CHOH—CH(C_2H_5)—CHO$, on distillation [72] at ordinary pressure is reported to be quantitatively dehydrated to the unsaturated aldehyde, $C_3H_7—CH{=}C(C_2H_5)—CHO$. With aldols possessing no hydrogen atoms on the α-carbon, there is no longer any chance for the simple dehydration reaction, and the other reaction of scission assumes major importance. Thus, the aldol from *iso*butyraldehyde [73] is quantitatively changed into the parent aldehyde by heating:

$$(CH_3)_2CH—CHOH—C(CH_3)_2—CHO \longrightarrow 2(CH_3)_2CH—CHO.$$

α,α-Dimethyl-β-hydroxy-butyraldehyde undergoes pyrolysis by distillation [74] at ordinary pressure into *iso*butyraldehyde and acetaldehyde. Some of the latter appears to change into crotonaldehyde during the process. α,α,δ-Trimethyl-β-hydroxy-caproic-aldehyde, $(CH_3)_2CHCH_2—CHOHC(CH_3)_2CHO$, even by distillation at 2 mm. pressure, breaks down to the two aldehydes, *iso*valeraldehyde and *iso*butyraldehyde.

[67] Grignard and Reif, *Bull. soc. chim.* [4] **1**, 116 (1907); Kyriakides, *J. Am. Chem. Soc.* **36**, 532 (1914).
[68] Wurtz, *Compt. rend.* **76**, 1166 (1873); **83**, 255 (1876); Nowak, *Monatsh.* **22**, 1140 (1901).
[69] Wurtz, *Compt. rend.* **97**, 1525 (1883).
[70] de Bruyn, *Bull. soc. chim.* [2] **42**, 164 (1884).
[71] Thalberg, *Monatsh.* **19**, 154 (1898).
[72] Weizmann and Garrard, *J. Chem. Soc.* **117**, 324 (1924).
[73] Usherwood, *J. Chem. Soc.* **123**, 1717 (1923).
[74] Lilienfeld and Tauss, *Monatsh.* **19**, 77 (1898).

α,α-Disubstituted-β-hydroxy acids behave also in this way. To illustrate (see p. 443):

$$CH_3CHOHC(C_2H_5)_2CO_2H\,[75]\ (\text{or } -CO_2Na) \xrightarrow{190^\circ} CH_3CHO + (C_2H_5)_2CHCO_2H\ (\text{or } -CO_2Na)$$

$$CH_3CHOHC(CH_3)(C_3H_7)-CO_2H\,[76] \longrightarrow CH_3CHO + C_3H_7CH(CH_3)-CO_2H,$$

at 170-200°, and apparently in good yields.

Tertiary Alcohols.

Tertiary Butyl Alcohol.

When vapors of this alcohol [77] are passed over pumice at 500°, the pyrolysis proceeds almost exclusively to *iso*butylene and water. From 30 grams of the alcohol, there results 6.5 grams of water (6.6 grams calculated), and enough butylene to form 59 grams of tertiary butyl iodide with HI (calculated, 74 grams). At 600°, secondary decompositions set in, and from 31.5 grams of tertiary butyl alcohol the following reaction products result;—(1) some carbonization; (2) about one liter of gas, the last 100 cc. of which is 67 percent methane, 29.3 percent hydrogen and 3.7 percent carbon monoxide; (3) six cc. of water; and 82 grams of olefine bromides, which on fractionation give 49.4 grams of *iso*butylene bromide, 13.9 grams of tribromobutane and a trace of tertiary butyl bromide.

Tertiary Amyl Alcohol.

Studied similarly [78] at 600-620°, tertiary amyl alcohol also reveals carbonization, the formation of 11.5 liters of gas, and the production of 45.2 cc. of distillate from 71.5 grams of the alcohol applied during 75 minutes. The gas is 70.2 percent methane, 19.5 percent hydrogen, 5 percent carbon monoxide and 5.3 percent ethane. The bromine tubes had previously removed the unsaturated hydrocarbons. The reaction gives 68.5 grams of crude olefine bromides, which are a mixture of ethylene, propylene and butylene bromides, together with 0.35 grams of butadiene tetrabromide and 8.7 grams of tri- and tetrabromobutane. Of the dibromides, 19.3 grams boil at 135-141°, an equal amount at 141-152°, and 8.4 grams at 152-166°. Of the 45.2 cc. of distillate, 12.3 cc. is water, about 7.5 cc. is unchanged alcohol, and 16 cc. is amylene, chiefly trimethylethylene. Possibly, as Nef suggests, the reason for the appearance of unused alcohol in this reaction and no

[75] Schnapp, *Ann.* **201**, 62 (1880).
[76] Jones, *Ann.* **226**, 287 (1884).
[77] Nef, *Ann.* **318**, 210 (1901).
[78] Nef, *ibid.*, p. 218.

unused alcohol in the reaction with tertiary butyl alcohol is because of a recombination of water with trimethylethylene on cooling, but a non-reaction of *iso*butylene and water under similar conditions. However, it would not be illogical to suppose that the recovered alcohol had never been decomposed.

Very probably, the first reaction to occur with tertiary amyl alcohol is a dehydration into trimethylethylene. Of the 0.73 mol of the alcohol which was not recovered, there results 0.68 mol of water. Only 0.16 mol of trimethylethylene is collected as such, but the opportunities for loss with this substance are great. Undoubtedly also, it undergoes pyrolysis into simpler substances. The data show the formation of 0.36 mol of methane, 0.10 of hydrogen, and 0.02 each of carbon monoxide and ethane. Possibly the ethane is formed by scission into acetone and ethane. With more complex tertiary alcohols this is a general reaction. The carbon monoxide is, no doubt, formed at least in part by the reaction of water vapor and carbon, a reaction which forms an equal quantity of hydrogen.

Methyl-2-Hexanol-2.

Methyl-2-hexanol-2, a tertiary alcohol which may be readily[79] synthesized from acetone and butyl magnesium bromide, may be distilled repeatedly under diminished pressure without decomposition; boiling point (20 mm.) 58-60°, and boiling point (50 mm.) 77-78°. A 140 gram portion of the pure alcohol, if heated at ordinary pressure,[80] gives the following results: a 5 gram fraction, consisting of two layers, boiling point 85-135°; a 20 gram fraction, also two layers, from 135-139°; 50 grams of methyl-2-hexanol-2 between 139-142; and about 60 grams between 142-153°, which is largely methyl-2-hexanol-2. Redistillation of the first two fractions yields about 4 grams of methyl-2-hexene-2, boiling point 92-94°, and 1 gram of water:

$$(CH_3)_2C(OH)—CH_2—C_3H_7 \longrightarrow H_2O + (CH_3)_2C{=}CH—C_3H_7.$$

If the alcohol is refluxed for 4 hours at atmospheric pressure, considerable water is formed, but much of the alcohol is still unchanged. At this temperature, there is no tendency for scission of the tertiary alcohol into a ketone and a hydrocarbon.

If this tertiary alcohol (48.5 grams) is refluxed[81] with a trace of

[79] Hurd, unpublished data. It has been made previously by Henry, *Compt. rend.* **143**, 103 (1906), from ethyl valerate and methyl magnesium bromide.

[80] Hurd and Bennett, unpublished data.

[81] Compare Hibbert, *J. Am. Chem. Soc.* **37**, 1748 (1915), who used this method to convert diacetone alcohol into mesityl oxide. *Also*, Brooks and Humphrey, *ibid.* **40**, 830 (1918), for secondary and tertiary alcohols with iodine catalyst.

iodine as a catalyst and then slowly distilled, two isomeric heptenes, methyl-2-hexene-2 and methyl-2-hexene-1, appear to be formed, but here again, much of the alcohol resists the treatment and is isolable as such.

By distilling[82] dimethyl-β-iodoethyl carbinol, $(CH_3)_2C(OH)—CH_2CH_2I$, at atmospheric pressure, there is formed iodine, hydrogen iodide, and a brown oil which contains *β-iso*amylenyl iodide, $(CH_3)_2C{=}CH—CH_2I$. With another tertiary alcohol,[83]

$$(CH_3)_2C{=}CH—CH_2CH_2C(C_6H_5)—CH_3,$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad OH$$

water is easily eliminated at 150° with the formation of the diene. It would be very surprising if this did not also undergo a ketonic scission (see below), but no reference to this was made.

Phenyl Dimethyl Carbinol, and Related Substances.

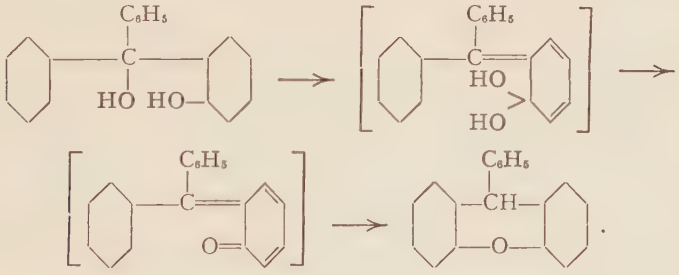
Phenyl dimethyl carbinol may be converted into β-phenyl propylene by thermal decomposition, and this is perhaps the most satisfactory method of preparation. It is only partially dehydrated[84] by one distillation, but with four repetitions of the process a 53 percent yield of the unsaturated hydrocarbon results. *Diphenyl methyl carbinol* is similarly converted[85] into unsymmetrical diphenyl ethylene in 58 percent yields by three distillations; boiling point of the ethylene, 268-275°. Both *phenyl α-naphthyl methyl carbinol* and *phenyl p-anisyl methyl carbinol* and *phenyl β-pyridyl methyl carbinol* are dehydrated to the unsaturated compounds by one distillation at diminished pressure. These methods are all to be recommended for the preparation of these substances. *Phenyl-2-butanol-2* becomes partially dehydrated even by vacuum distillation, but *phenyl p-tolyl methyl carbinol* is best dehydrated by three distillations at atmospheric pressure (278-294°). Methyl di-*p*-dimethylaminophenyl carbinol,[86] $((CH_3)_2NC_6H_4)_2C(OH)—CH_3$, in like manner, gives the unsaturated compound on heating, and the analogous methyl di-*p*-aminophenyl carbinol loses its water at 130°.

Ziegler has shown that an excellent way to synthesize tetraphenyl allene and related compounds is to heat tertiary alcohols of the type, $\Phi_2C{=}CH—C\Phi_2OH$, to 140-150°. This novel allene synthesis[87] has been used for tetraphenyl allene, $(C_6H_5)_2C{=}C{=}C(C_6H_5)_2$; for

[82] Spaeth and Spitzy, *Ber.* **58**, 2273 (1925).
[83] Helferich and Gehrke, *Ber.* **54**, 2640 (1921).
[84] Hurd and Webb, *J. Am. Chem. Soc.* **49**, 549 (1927).
[85] *See* "Organic Syntheses," VI, 32.
[86] Fecht, *Ber.* **40**, 3902 (1907).
[87] Ziegler and others, *Ann.* **434**, 74 (1923); *Ber.* **55**, 2274 (1922).

$(C_6H_5)_2C{=}C{=}C(C_6H_3(OCH_3)_2)—C_6H_4OCH_3$, and for $(C_6H_5)_2C{=}C{=}C(C_6H_4)_2O$. In the latter case, a quantitative yield was reported after one to two hours' heating on the water bath. In all cases the yields were good, but with $(C_6H_5)_2C{=}C{=}C(C_6H_4OCH_3)_2$ the allene was difficult to purify. Thinking that this method could be adapted for the synthesis of allenes with basic substituents,[88] Hurd and Webb attempted, but without success, to dehydrate phenyl-1-α-naphthyl-1-β-pyridyl-3-butene-1-ol-3, $C_{10}H_7—C(C_6H_5){=}CH—C(OH)(C_5H_4N)—CH_3$. At 160-170°, it changes into a dark mass that cannot be purified. Nor was it possible to prepare 1,3-diphenyl-1-α-naphthyl-3-p-dimethylaminophenyl-allene by the dehydration of a corresponding tertiary alcohol.

Apparently, triphenyl carbinol has not been studied for its pyrolysis. The o-hydroxy derivative gradually changes[89] through a quinonoid carbinol and a fuchsone structure into a xanthone:



Xanthones have similarly been formed when naphthyl radicals have replaced the phenyl radicals. Compounds of this type differ from the ordinary tertiary alcohol by having no hydrogen on the α-carbon atoms.

Penta-substituted Ethanols.

This branch of tertiary alcohols is interesting since they yield three distinct types of decomposition[90] by distillation at ordinary pressure. The first type is ordinary dehydration, due to the presence of a hydrogen atom on the carbon atom next to the hydroxyl. The following compounds all have the general formula $R_3C—C(Ar)(OH)—CH_2R$, and will become dehydrated or

[88] Hurd and Webb, *J. Am. Chem. Soc.* **49**, 554 (1927).
[89] Gomberg and McGill, *J. Am. Chem. Soc.* **47**, 2394 (1925).
[90] Ramart-Lucas, *Ann. chim.* [8] **30**, 349 (1913).

partially so by simple heating: $(CH_3)_3C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$ (Ref. 90, pp. 354, 383, Ramart-Lucas), $(CH_3)_3C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{C}}}}-OH$ (pp. 359, 388), $(CH_3)_2C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$ (p. 372), $(CH_3)_3C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_2C_6H_5}{\overset{|}{\underset{|}{C}}}}-OH$ (p. 394), and $(C_2H_5)_3C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$ (p. 404).

In all cases, the olefine formed possesses the structure, $R_3C-\overset{\displaystyle Ar}{\overset{|}{C}}=CH-R$.

A second type of such tertiary alcohols has the general structure, $R_2C-\overset{\displaystyle C_6H_5}{\underset{\displaystyle Ar}{\overset{|}{\underset{|}{C}}}}-OH$. With two aromatic groups on the α-carbon, there would seem to be no opportunity for olefine formation, yet water is eliminated by distillation with the resultant production of a hydrocarbon. To explain the formation of the compound produced, Mme. Ramart-Lucas postulated a transitory cyclopropane derivative, caused by loss of water between the hydroxyl and the methyl groups; then a subsequent rearrangement into $ArCR_2-\overset{\displaystyle C_6H_5}{\overset{|}{C}}=CH_2$. This type of reaction was postulated for diphenyl tertiary-butyl carbinol (Ref. 90, p. 390), and her mechanism would lead to the structure, diphenyl-2,3-methyl-3-butene-1, $C_6H_5C(CH_3)_2-\overset{\displaystyle C_6H_5}{\overset{|}{C}}=CH_2$. However, recent work by Marvel and Bateman [91] indicates that the structure of the hydrocarbon formed by the dehydration of this carbinol is diphenyl-3,3-methyl-2-butene-1, and this is the structure one would expect if the carbinol underwent a Wagner rearrangement. Thus,

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}-\overset{\displaystyle OH}{\overset{|}{C}}(C_6H_5)_2 \longrightarrow CH_3-\overset{\displaystyle CH_2}{\overset{\|}{C}}-C(C_6H_5)_2 + H_2O.$$

Another pentasubstituted ethanol, namely, phenyl *p*-tolyl tertiary-butyl carbinol was dehydrated by a mixture of acetic anhydride and acetyl chloride, but whether or not the same could have been effected by heat

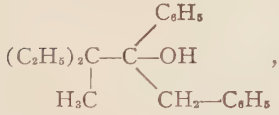
[91] Bateman with Marvel, *J. Am. Chem. Soc.* **49**, 2915 (1927).

alone was not stated. A good summary of recent hypotheses regarding the mechanism of the Wagner rearrangement is given in the Annual Reports of the London Society, **21**, 96 (1924).

A third type of pentasubstituted ethanols differs from the other two in that there is no dehydration by heat, but instead scission into a ketone and a hydrocarbon. To illustrate this, distillation of diphenyl triethyl-methyl carbinol, $(C_2H_5)_3C—C(C_6H_5)_2—OH$, at ordinary pressure yields [92] triethyl-methane and benzophenone, quantitatively. The following is a general reaction:

$$R_3C—CAr_2—OH \longrightarrow R_3CH + Ar_2CO,$$

in case not more than one of the R groups is methyl. Thus, (*ibid.* p. 374), benzophenone and diethyl-methyl-methane are formed by distilling methyl-2-ethyl-2-diphenyl-1,1-butanol-1, $(C_2H_5)_2C(CH_3)—C(C_6H_5)_2—OH$. It is rather curious to note that the benzyl analog,



, behaved similarly (pp. 376, 400). Instead of dehydration, there is formed diethylmethylmethane and desoxybenzoin. The carbinol may be readily dehydrated, however, by a mixture of acetic anhydride and acetyl chloride. Distillation of pentaphenyl-ethanol [93] in a vacuum gives a volatile portion which is almost pure triphenylmethane, and a charred residue which is partly soluble in benzene.

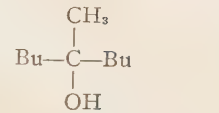
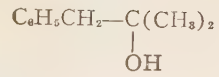
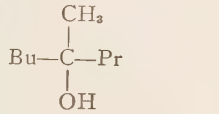
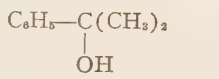
Grignard [94] has recently shown that unsaturated as well as saturated tertiary alcohols of various types undergo ketonic fission during distillation. In general, as the temperature of distillation increases, the effect of the dehydration reaction diminishes and the ketonic decomposition comes more and more into play, so that at 650-700° the latter is almost the exclusive reaction except for charring. However, with brick-dust or pumice, only dehydration occurs. The best conditions for the production of the ketones without charring is to use diminished pressure and a temperature of 400-500°, with or without the presence of glass wool.

Since in these cases, there is a breaking of the carbon-to-carbon bond, the results offer a means of determining the relative electro-negativity of the different radicals united to the tertiary carbon. Obviously, the group with the least "affinity capacity" should form the

[92] Ramart-Lucas, *loc. cit.*, p. 377.
[93] Schmidlin and Wohl, *Ber.* **43**, 1149 (1910).
[94] Grignard and Escourrou, *Compt. rend.* **176**, 1860 (1923); Grignard and Dubien, *Ann. chim.* [10] **2**, 298 (1924); Grignard and Chambret, *Compt. rend.* **182**, 299 (1926).

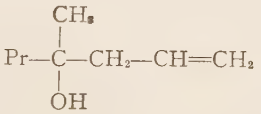
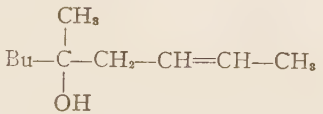
TABLE XXI. *Formation of Ketones from Alcohols by Pyrolysis.*

Saturated Alcohols

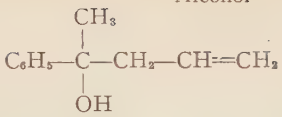
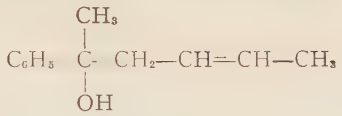
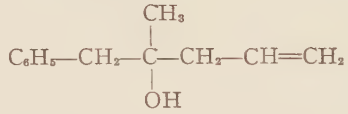
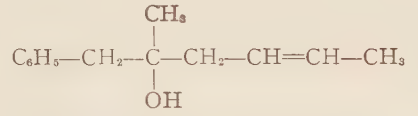
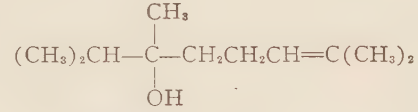
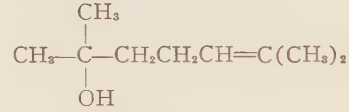
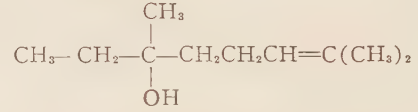
Alcohol	Ketone Formed	Percent Yield
	$Bu-CO-CH_3$	30
	$(CH_3)_2CO$	60
	unidentified mixture	
	$C_6H_5COCH_3$*	80

Unsaturated Alcohols

Unsaturation β to the Carbinol

	$Pr-CO-CH_3$	50 60–65 (500°, 160 mm.)
	$Bu-CO-CH_3$	30

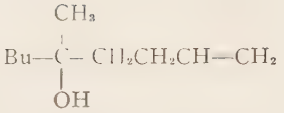
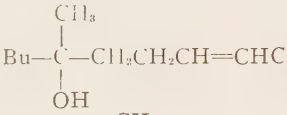
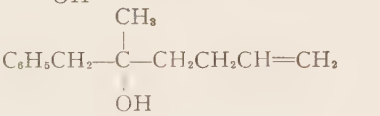
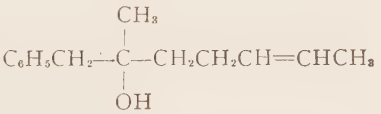
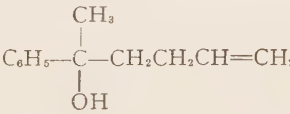
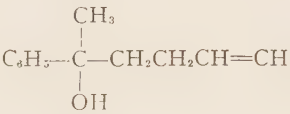
* Compare p. 168, for the dehydration reaction at lower temperatures.

Alcohol	Ketone Formed	Percent Yield
	$C_6H_5—CO—CH_3$	80
	$C_6H_5—CO—CH_3$	80
	$C_6H_5—CH_2—CO—CH_3$	60 90 (400-450°, 30 mm.)
	$C_6H_5—CH_2—CO—CH_3$	60–65 90 (400°, 30 mm.)
Unsaturation γ to the Carbinol		
	$CH_3—CO—CH_2CH_2CH=C(CH_3)_2$ + propane †	75 (12 mm.)
	Very slight fission †	
	Very little fission †	

† Saturated alcohols of these three types also give very little fission.

TABLE XXI—(*Continued*).

Unsaturation γ to the Carbinol—(*Continued*).

Alcohol	Ketone Formed	Percent Yield
	$CH_3—CO—CH_2CH_2CH=CH_2$	20–30
	$CH_3—CO—CH_2CH_2CH=CHCH_3$	50
	$CH_3—CO—CH_2CH_2CH=CH_2$	50–60
	$CH_3—CO—CH_2CH_2CH=CHCH_3$	50–60
	$C_6H_5—CO—CH_3$ ‡ and also $CH_3COCH_2CH_2CH=CH_2$	50
	$C_6H_5—CO—CH_3$ ‡ and also crotyl-acetone.	50–60

‡ In the last two cases, at 400° and 30 mm. there is also a noticeable dehydration.

Unsaturation α to the Carbinol §

Alcohol	Ketone Formed	Percent Yield
$C_6H_5-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH=CH-CH_2CH_2CH_3$	$C_6H_5COCH_3$ and pentene (12 mm. pressure). At atmospheric pressure, water is eliminated by heating.	
$C_6H_5-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH=CH-C_6H_{13}(n)$	$C_6H_5COCH_3$	Evidently in good yields, if done *in vacuo*.
$C_6H_5CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH=CH-C_6H_{13}(n)$	$CH_3COCH=CH-C_6H_{13}(n)$	A little less abundantly. Done *in vacuo*.

§ The ketonic scission with the α proceeds less smoothly than with the β or γ, because of the greater dehydrating tendency.

hydrocarbon. The results indicate the following series: phenyl > methyl > γ-ethylenic > benzyl, or aliphatic radical above methyl > β-ethylenic. The α-ethylenic radicals, in the cases studied, seem to resemble the γ-ethylenic radicals closely, but side reactions occur more easily.

Table XXI gives in each case the alcohol used, the ketone formed and its yield. The temperature is 600°, and the pressure atmospheric unless otherwise stated.

In all of these cases, phenyl is consistently the most electronegative radical, since it remains attached to its valence electrons and always appears in the ketone. The formation of heptaldehyde from castor oil (p. 164) is another reaction of this type with a secondary alcohol instead of a tertiary. Another tertiary alcohol which behaves similarly is α,α,β-triphenyl-β-amino-ethanol; this changes into benzophenone and benzyl amine at 150-180°, but better yields [95] result when the substance is heated in a sealed tube at 120-200° with water.

$$C_6H_5CHNH_2—C(C_6H_5)_2—OH \longrightarrow C_6H_5CH_2NH_2 + (C_6H_5)_2CO.$$

Similarly, diphenyl-aminomethyl-carbinol yields benzophenone and methyl amine; dibenzyl aminomethyl carbinol yields dibenzyl ketone and methyl amine; and α,α-dibenzyl-β-phenyl-β-amino-ethanol appears to give benzyl amine and dibenzyl ketone.

Poly-hydric Alcohols.

Glycols.

Ethylene Glycol. This is remarkably resistant to heat. It may be passed over pumice [96] at 400° without decomposition. The use of glycol as an anti-freeze for automobile radiators is, in a measure, dependent on this property. Glycol starts to decompose at 500-520°, and at 550° the decomposition is rapid Even so, 14.4 grams of it may be recovered from an original 40 gram. The decomposition products are acetaldehyde (7 cc.), water (5 cc.), some crotonaldehyde (traces), and gas (4.5 liters). The gas is 50 percent carbon monoxide, 11.5 percent hydrogen, and the remainder methane. No unsaturated hydrocarbons are present. The obvious conclusion from this experiment is that the major products of the reaction are acetaldehyde and water:

$$CH_2OH—CH_2OH \longrightarrow CH_3—CHO + H_2O.$$

The chief secondary reaction is the pyrolysis of acetaldehyde into carbon dioxide and methane.

[95] Bettzieche and Ehrlich, *Z. physiol. Chem.* **150**, 191 (1925).
[96] Nef, *Ann.* **335**, 200 (1904).

Propylene Glycol. When propylene glycol is passed over pumice at 500°, it gives 20.8 cc. of distillate from 26 grams of the original glycol. Propionaldehyde is the major component of this distillate; 13.1 cc. boils between 52-75°. It is important to note that acetone is definitely not a product of this reaction. Therefore, the reaction cannot proceed through the intermediate step of propylene oxide, since this gives both propionaldehyde and acetone (ratio of 2:1) under similar conditions. Nef passed his propylene glycol (26 grams) through the furnace in 165 minutes.

Higher Glycols. Among higher glycols, it may be mentioned in passing that Kyriakides[97] has made a fairly thorough study of the catalytic dehydration of various glycols at high temperatures. With a clay catalyst,[98] a 70 percent yield of methyl isoprene is reported to come from pinacol at 400°.

It appears that the conversion of a glycol into an aldehyde or ketone depends on the temperature for the final product. Thus, at 250-300° the compounds $(C_6H_5)_2C(OH)—CH_2OH$ and $(C_6H_5)(C_2H_5)C(OH)—CH_2OH$ give the aldehydes[98a] exclusively, whereas at 400-450° the same glycols give the ketones exclusively. Hydrobenzoin, $C_6H_5—CHOH—CHOH—C_6H_5$, changes into diphenyl-acetaldehyde at 250-300°, whereas either of these two substances gives phenyl benzyl ketone as the chief product at 400-450°. Benzaldehyde is also produced during the pyrolysis of hydrobenzoin.

The dehydration of glycols into aldehydes, ketones or dienes is not the only type of reaction to be expected in the heating of such bodies. It is noteworthy that ethylene oxides are not formed by this reaction. However, benzopinacol, $(C_6H_5)_2C(OH)—C(OH)(C_6H_5)_2$, may be an exception to this statement. At 200°, a very poor yield[99] of α-benzopinacoline, $(C_6H_5)_2C(O)C(C_6H_5)_2$, is reported to be formed. In the latter case, and in other tetraaryl glycols the major reaction certainly follows quite a different course, namely, that of scission into a ketone and an alcohol. Thus, benzopinacol breaks down,[100] nearly completely, at its melting point (185°) into benzophenone and benzohydrol:

$$(C_6H_5)_2C(OH)—C(OH)(C_6H_5) \longrightarrow (C_6H_5)_2CO + (C_6H_5)_2CHOH.$$

[97] Kyriakides, *J. Am. Chem. Soc.* **36**, 980 (1914).
[98] D. R. P. 235,311, Dec. 2, 1910, *Chem. Zentr.* **1911**, II, 112; *see also*, Weber, *Ind. Eng. Chem.* **18**, 405 (1925); Duisberg, *Z. elektrochem.* **24**, 369 (1918).
[98a] Ramart-Lucas and Salmon-Legagneur, *Compt. rend.* **186**, 1848 (1928).
[99] Delacre, *Ann. chim.* [9] **12**, 396 (1919).
[100] Thörner and Zince, *Ber.* **10**, 1473 (1877).

The homolog, $CH_3C_6H_4C(OH)(C_6H_5)—C(OH)(C_6H_5)—C_6H_4CH_3$, behaves analogously at its melting point, 165°. The decomposition products are phenyl tolyl ketone and phenyl tolyl carbinol. In contrast to these results, hydrobenzoin, $C_6H_5—CHOH—CHOH—C_6H_5$, boils above 350°, showing that disubstituted compounds are more stable. Pinacol, itself, pyrolyzes [101] into acetone and *iso*propyl alcohol by passing it through a red hot tube filled with pieces of glass. The yields are not stated. Finally, tetraphenyl-benzopinacol, [102] at 200-203°, melts with decomposition into equivalent amounts of dibiphenyl ketone and dibiphenyl carbinol:

$$(C_{12}H_9)_2C(OH)—C(OH)(C_{12}H_9)_2 \longrightarrow (C_{12}H_9)_2CO + (C_{12}H_9)_2CHOH.$$

The distillation of certain aryl dialkyl glycols [103] induces aldehyde formation, and there is evidence to support Tiffeneau's view that water is first eliminated following which the aryl group "wanders", and not the reverse order. This evidence is obtained by studying the pyrolysis

$$Ar—CHOH—C(OH)R_2 \longrightarrow \left[Ar—CH(O)—CR_2\right] \longrightarrow CH(Ar)—C(=O)R_2$$

of similar ethylene oxide derivatives, which will be discussed shortly. Anisyl-dimethyl-glycol gives anisyl-dimethyl-acetaldehyde at 300°, and anisyl-diethyl-glycol pyrolyzes into anisyl-diethyl-acetaldehyde by distillation:

$$CH_3OC_6H_4CHOH—C(OH)(C_2H_5)_2 \longrightarrow O{=}CH—C(C_2H_5)_2(C_6H_4OCH_3) + H_2O.$$

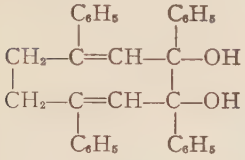
However, no such rearrangement is noticed with phenyl-dibenzyl-glycol, $C_6H_5CHOH—C(OH)(C_7H_7)_2$. It seems that the tertiary hydroxyl increases in stability as the alkyl radicals become heavier. The effect of heat on diphenyl-1,4-anisyl-3-butandiol-2,3,

$$C_6H_5CH_2—CHOH—C(OH)(C_6H_4OCH_3)—CH_2C_6H_5$$

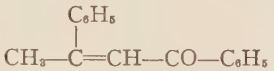
is to cause the formation of diphenyl-1,4-anisyl-3-butanone-2; no aldehyde is produced in this case.

[101] Thörner and Zincke, *Ber.* **13**, 645 (1880).
[102] Gomberg and Bachmann, *J. Am. Chem. Soc.* **49**, 252 (1927).
[103] Tiffeneau and Levy, *Bull. soc. chim.* **33**, 735 (1923); **39**, 763 (1926); *Compt. rend.* **183**, 1112 (1926); Tiffeneau, Orekhoff and Levy, *ibid.* **179**, 977 (1924).

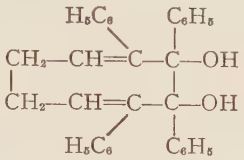
Dypnopinacol [104] is an α-glycol which is assigned the following formula.



Dypnopinacol

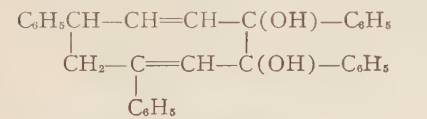


Dypnone

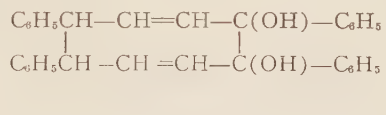


Luteo-Dypnopinacol-γ

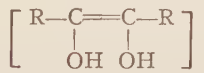
It is a polymerization product of dypnone, into which it reverts in 70 percent yields by distillation (200-250°). Merely by fusion of dypnopinacol (*Ann. Chim.* [9] **12**, 409), cooling and extraction of the unchanged material by crystallization from alcohol, there is about a 6.2 percent isomerization into luteo-dypnopinacol-γ. Delacre believes that the action of heat on dypnopinacol effects either depolymerization or isomerization, depending on the temperature. Within the limits of experimental error, there is no dehydration. In a further study, in which 50 grams is heated for 4.5 hours at 190° in a vacuum,[105] homodypnopinacol, and homodypnopinacol-α and -β may be isolated.



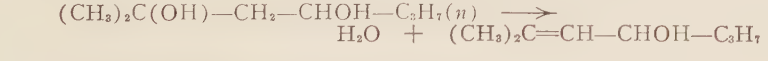
Homodypnopinacol



Homodypnopinacol-α and -β

Unsaturated compounds of the type  are too unstable [106] to isolate. Compounds which might be expected to contain this functional group, possess instead, the formula, R—CO—CHOH—R.

Other Glycols. Distillation of methyl-2-heptanediol-2,4 at ordinary pressure [107] gives chiefly methyl-2-heptene-2-ol-4:



but also a portion of it becomes completely dehydrated into a mixture of octadienes. In addition there is some higher boiling material, probably formed by the polymerization of some erythrene, which is simultaneously produced. The homolog of this diol, methyl-3-octanediol-3,5, behaves in precisely the same manner. The chief product of the distillation is methyl-3-octene-3-ol-5, but hydrocarbons also accompany this.

By maintaining pentanediol-1,4 for a time above its boiling point [108]

[104] Delacre, *Ann. chim.* [9] **2**, 81 (1914); **12**, 396 (1919).
[105] *Ibid.* **12**, 152, 396.
[106] Klinger and Standke, *Ber.* **24**, 1270 (1891).
[107] Grignard and Dubien, *Ann. chim.* [10] **2**, 314 (1924).
[108] Perkin, Jr., and Freer, *Ber.* **19**, 2568 (1886).

(210-220°), the anhydride is formed (boiling point 78-83°), together with an appreciable amount of higher boiling residue. A better method of dehydration is the use of 50 percent sulfuric acid at 100°.

$$CH_3—CHOH—CH_2CH_2CH_2OH \longrightarrow CH_3—CH—(CH_2)_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

Trimethylene Glycol. The quantity of gaseous products from trimethylene glycol, $CH_2OH—CH_2CH_2OH$, at 450° over pumice,[109] is very small. Only one liter of gas is produced from 60 grams of the glycol (in 5 hours), and this is mainly entrained air. Some liquid products are formed, but 38 grams of the glycol is recoverable, which, if again subjected to pyrolysis (4 hours, 480°), may be further decomposed. In this manner, 32.1 grams of material which boils lower than trimethylene glycol (50-103°), and 3.1 grams which boils higher, may be prepared while 11 grams is still undecomposed. The lower boiling portion consists of acrolein (10.5 cc.), traces of propionaldehyde, allyl alcohol (4 cc.), *n*-propyl alcohol (4 cc.), and the remainder water. For Nef's interpretation of this reaction, see p. 19. A simpler mechanism is given there also, which is based on the primary dehydration of trimethylene glycol into allyl alcohol, and its subsequent breakdown.

Vacuum distillation[110] of ω-dihydroxymethyl-α-picoline causes water elimination, giving pyridyl allyl alcohol:

$$\alpha C_5H_4N—CH(CH_2OH)_2 \longrightarrow H_2O + CH_2=C—CH_2OH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_5H_4N$$

In this experiment, the temperature of the liquid is 170-177°, and of the vapor, 135-140°. Apparently, the yields are good, although they are not stated.

Terpin hydrate possesses two tertiary and one primary alcohol groups, and in addition two of these hydroxyls are on the 1,3 carbon atoms as in trimethylene glycol. The mode of decomposition during distillation (258°) is, however, dependent on other factors, since a ring-closure[111] occurs with the formation of *cis*-terpin. The two tertiary groups are unchanged.

$$(CH_3)_2C(OH)—CH_2CH_2CH_2C(OH)—CH_3 \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\quad HOCH_2—CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2—CH_2$$
$$(CH_3)_2C(OH)—CH\qquad\qquad\qquad\qquad\qquad\qquad C(OH)—CH_3 + H_2O$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2—CH_2$$

[109] Nef, *Ann.* **335**, 206 (1904).
[110] Lipp and Richard, *Ber.* **37**, 742 (1904).
[111] Wallach, *Ann.* **230**, 248 (1885).

Renshaw [112] has determined that dibromohydrin, $CH_2Br—CHBr—CH_2OH$, breaks up completely at the temperature of boiling thymol, but at 100° this dissociation is slight. One of the products is hydrogen bromide.

For the pyrolysis of the polyols, related to the carbohydrates, such as mannitol, see the chapter on carbohydrates.

Ethylene Oxide Derivatives.

The rather intimate relationship between the glycols and the ethylene oxide derivatives makes it advisable to treat the latter at this point. Ethylene oxide itself rearranges [96] into acetaldehyde at 400-420°, and in the presence of alumina this rearrangement [113] occurs at 200°. Quite recently, Peytral [114] has reinvestigated this reaction, and if the vapors of the oxide are rapidly passed through a hot tube, three simultaneous reactions are found to occur. The decomposition is an exothermic one, the temperature of the gas rising in 0.002 second from 571° to 1200°. Of the three reactions, given below, 56 mols per 100 mols of the oxide pyrolyze according to the first equation; 34 mols, according to the second equation; and 10 mols, according to the third equation.

$$4(CH_2)_2O \longrightarrow 4HCHO + C_4H_8$$
$$(CH_2)_2O \longrightarrow CH_3—CHO$$
$$(CH_2)_2O \longrightarrow C_2H_2 + H_2O$$

The side reactions include the pyrolysis of formaldehyde into carbon monoxide and hydrogen; of acetaldehyde into carbon monoxide and methane; and the partial reduction of acetylene into ethylene or methane. The gas analysis reveals 44.7 percent carbon monoxide, 28.3 percent hydrogen, 15 percent methane, 7 percent butylene, and 5 percent acetylene.

Ipatiew [113] indicated 500° as the temperature when both ethylene oxide and propylene oxide start to decompose. At this temperature, he found the products of the reaction to include not only aldehydes and ketones (see p. 177), but also their decomposition products. He recommended the use of alumina to inhibit the side reactions, because of the lower temperature of the reaction. Amylene oxide, $CH_2—C(CH_3)—C_2H_5$ (O), is stable in glass tubes at 300°, but at 500° the pyrolysis starts. From 23 grams of material, passed during 135 minutes, there is very little gas and a quantity of liquid distillate, boiling point 86-98° (the original

[112] Renshaw, *J. Am. Chem. Soc.* **36**, 538 (1914).
[113] Ipatiew and Leontowitsch, *Ber.* **36**, 2017 (1903).
[114] Peytral, *Bull. soc. chim.* **39**, 206 (1926).

oxide has a boiling point of 73-76°), which is chiefly a mixture of aldehyde and ketone. At 600° (glass tube; 50 minutes), 22 grams of the oxide yields 6 liters of gas and 10 grams of distillate. The gas consists of 32.3 percent olefines, 20.6 percent carbon monoxide, 0.6 percent carbon dioxide, and 37.5 percent hydrogen and paraffins. The liquid, boiling point 50-100°, is a mixture of methyl *iso*propyl ketone and methylethylacetaldehyde.

As would be anticipated, the effect of prolonged heating at a low temperature is far different from the effect of short heating at high temperatures, and Levene and Walti have reported [115] that propylene oxide changes into a mixture of substances by heating for four weeks at 165-167° in a sealed tube. From 8 cc. at the outset, two-thirds was still unchanged and about 1 cc. was identified as the diether of propylene glycol, $CH_3—CH(—O—CH_2—CH_3)—O—CH_2$. By heating glycidol at 100° for 42 hours again there is much unchanged material, but a dimer is formed in yields of 3.5 grams from 30 grams in accordance with the following equation:

$$CH_2(O)CH—CH_2OH + HO—CH_2—CH(O)CH_2 \longrightarrow CH_2—O—CH_2—CHOH—CH_2OH \quad CH_2(O)CH_2$$

By heating at 125° for several days, a higher condensation product was also obtained. Nef observed the formation of a sweet tasting resin when glycidol is heated for 2 hours at 200°. (See p. 185 for the data on the pyrolysis of glycidol [116] at higher temperatures.)

With kaolin and diminished pressure,[117] homologs of ethylene oxide may be readily dehydrated into butadienes at 450°. Thus:

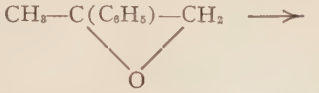
$$R_2C(O)CR—CHR—CHR_2 \ (R \text{ may} = H) \longrightarrow R_2C{=}CR—CR{=}CR_2 + H_2O.$$

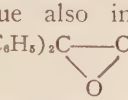
Thirty grams of pure isoprene may be synthesized in this way from 100 grams of methyl butylene oxide. Some methyl-butanal is also formed, but it is probably not an intermediate product, since it pyrolyzes at a higher temperature into isoprene (with kaolin), namely 500-550°, and gives a much smaller yield of isoprene.

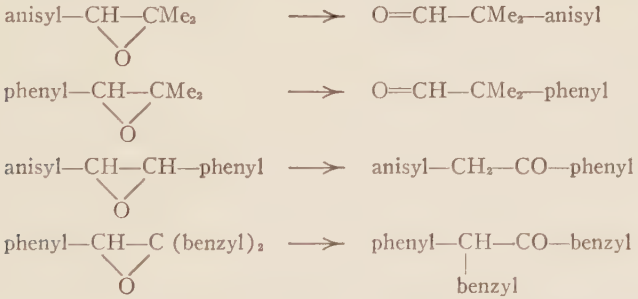
The distillation of phenyl-propylene-oxide [118] (from a small flask

[115] Levene and Walti, *J. Biol. Chem.* **75**, 325 (1927).
[116] Nef, *Ann.* **335**, 232 (1904).
[117] Kyriakides, *J. Am. Chem. Soc.* **36**, 657, 663 (1914).
[118] Danilov and Danilova, *Ber.* **60**, 1061 (1927).

in which are inserted a few pieces of ignited clay plate) causes a 91 percent rearrangement into α-phenyl-propionaldehyde:



The rupture of the carbon-to-oxygen bond, therefore, appears to occur on the side nearer to the more electronegative radical. This is true also in the case [119] of α-methyl-β,β-diphenyl-ethylene oxide,  , which, by slow distillation at atmospheric pressure, gives unsymmetrical diphenyl acetone exclusively. This involves a wandering of the hydrogen atom. The homolog, α-ethyl-β,β-diphenyl-ethylene oxide, also undergoes a similar change into ethyl-benzohydryl ketone, but in this case there is also a minor rearrangement into α,α-diphenyl-butyraldehyde. Thus, there is somewhat of a tendency for the ethyl group to wander as well as the hydrogen. In general, hydrogen has a greater tendency to migrate than alkyl radicals [120] if there is a choice, but in the case of the tendency of aryl radicals to migrate in preference to the hydrogen radical, there is no fixed rule. The following equations illustrate this.



Thus, if it is accepted that the rupture of the oxygen bond in the oxides occurs on the side nearer to the radical with the greater electron attraction, it is obvious that the affinity capacity of the phenyl group, increased by that of hydrogen, is less than that of two methyls but greater than that of two benzyls. Furthermore, as has been shown in Chapter 2 (p. 38), anisyl possesses more electron attraction than phenyl.

A rather peculiar course is followed in the distillation of 1,2-diphenyl

[119] Levy and Lagrave, *Compt. rend.* **180**, 1032 (1925).
[120] Tiffeneau and Levy, *Bull. soc. chim.* **39**, 763 (1926); *Compt. rend.* **182**, 391 (1926); Tiffeneau, Orekhoff and Levy, *ibid.*, **179**, 977 (1924).

ethylene oxide, $C_6H_5CH—CH—C_6H_5$ (O); instead of producing desoxybenzoin, the products are benzaldehyde and stilbene.

Lagrave [120a] has investigated the behavior of alkyl diphenylethylene oxides, which may be prepared by the interaction of benzoyl hydroperoxide and the corresponding olefine. In the rearrangement to the ketone or aldehyde, either the hydrogen radical or the alkyl radical respectively must wander to the carbon atom with two phenyl groups attached. Thus:

$$(C_6H_5)_2C—CHR \text{ (O)} \rightarrow (C_6H_5)_2CH—CO—R$$
$$(C_6H_5)_2C—CHR \text{ (O)} \rightarrow (C_6H_5)_2CR—CHO$$

When R represents methyl or phenyl, the ketone is the exclusive rearrangement product, and this is the case also with *n*-propyl. With ethyl, however, the ratio of the ketone to the aldehyde is 85 to 15; with *iso*propyl, 82 to 18; with *iso*butyl, 80 to 20; with *n*-butyl, 77 to 23; and with benzyl, 42 to 58. The greater tendency for the benzyl group to wander, as compared with other alkyl groups, is significant. Lagrave considers that these rearrangements to aldehydes or ketones are one-phase processes, since at the temperatures employed there was no tendency for the aldehyde to rearrange to the corresponding ketone.

Glycidol, the ethylene oxide compound related to glycerol, will be discussed again after glycerol has been presented.

Glycerol.

It has been observed [121] that either diglycerol, $(C_3H_7O_2)_2O$, or polyglycerols, result when glycerol is heated for a period of 7-8 hours at 290-295°. If glycerol vapors are passed [122] over a glowing platinum spiral, formaldehyde, glyoxal and acrolein are produced.

The most thorough study of the pyrolysis of glycerol [123] is that of Nef. He observed considerable decomposition at 430-450° in a pumice-filled tube, thereby showing it to be less resistant to heat than ethylene glycol. If glycerol is added at the rate of 4 drops per minute, 250 grams will have passed the hot tube in 16 hours. This rate was used by Nef, and he reported much graphite in the tube; a liquid distillate representing 90 percent by weight of the glycerol; and an inappreciable volume of gases (only 1.9 liters from 200 grams of glycerol). Analysis of the last 98 cc. of gas indicated 80.3 cc. of carbon monoxide and 12.4 cc.

[120a] Lagrave, *Ann. chim.* **8**, 363 (1927).
[121] Will, *Chem. Zentr.* **1906**, II, 1000; **1907**, II, 199; Claessen, D. R. P. 181,754.
[122] Trillat, *Bull. soc. chim.* [3] **29**, 42 (1903).
[123] Nef, *Ann.* **335**, 209 (1904).

of hydrogen. Fractionation of the brown-colored distillate gave five fractions.

(1) 28.8 grams of a volatile portion consisting of formaldehyde, acetaldehyde and acrolein.
(2) 48 grams of a 20 percent solution of hydroxy-acetone (acetol) in water, boiling point$_{15}$ 23-40°.
(3) 9 grams of almost pure acetol, boiling point$_{15}$ 40-60°.
(4) 25.1 grams of a mixture of formaldehyde-glycerol, $HO—C_3H_5<\begin{matrix}O\\O\end{matrix}>CH_2$, acetaldehyde-glycerol, and acrolein-glycerol (the latter two with similar structures to the first), boiling point$_{15}$ 75-110°. About half of this fraction was acetaldehyde-glycerol, boiling between 85-96°.
(5) A fraction having the boiling point (15 mm.) 170°. It consisted of 66 grams of unchanged glycerol and 11.4 grams of residue.

Thus, the pyrolysis may be traced in the following steps:

$$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix} \longrightarrow \begin{matrix}CH_3\\|\\CO\\|\\CH_2OH\end{matrix} \quad \text{and} \quad \begin{matrix}CH_2\\\|\\CH\\|\\CHO\end{matrix},$$

$CH_3—CHO$, HCHO, and the reaction products of these aldehydes with glycerol. The mechanism of the formation of acetol from glycerol is not known with certainty, but the simultaneous oxidation and reduction of adjacent carbon atoms is not an unfamiliar reaction in organic chemistry. The source of the formaldehyde and the acetaldehyde is acetol; see p. 158. No glycidol is formed by the thermal decomposition of glycerol.

Glycidol.

Although permanently stable at room temperature, glycidol,[124] $HOCH_2—\begin{matrix}CH\\|\\CH_2\end{matrix}>O$, becomes converted into a sweet-tasting resin when heated for two hours at 200°. The pyrolysis follows a different course, however, if the vapors are heated at a higher temperature. At a rate of 8 grams per hour, glycidol decomposes at 450° over pumice to give 6.7 liters of gas in 3.5 hours. The analysis of the gas follows: carbon monoxide 58.2 percent, hydrogen 18.1 percent, methane 23.7 percent. There is much carbonization in the tube. In 5 hours, 23 grams of a strongly-smelling oil, 9 cc. of which is acetaldehyde (boiling point 29-45°) is collected. The higher boiling components are: 1.5 cc. of water and crotonaldehyde thought to be formed from acetaldehyde at 400-500° (boiling point 85-95°); 2.7 grams of water and acetol (boiling

[124] Nef, *ibid.*, p. 232.

$point_{20}$ 40-55°); 3.2 grams of acetol (boiling point 55-60°); and 4.5 grams of residue which began to decompose and deposit metaformaldehyde in the receiver.

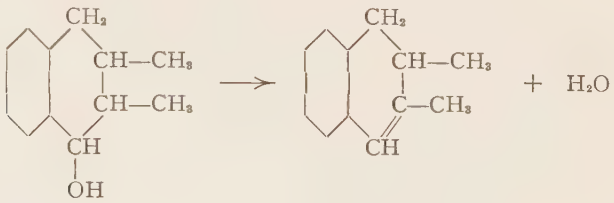
At best, no more than traces of acrolein are formed from glycidol, although the temperature of the reaction was sufficiently great to decompose much of the hydroxy-acetone into formaldehyde and acetaldehyde.

Cyclic Alcohols.

By analogy with the aliphatic alcohols, it would be anticipated that cyclohexanol would undergo pyrolysis at sufficiently high temperatures into cyclohexene and water, or into cyclohexanone and hydrogen. The customary method [125] of preparing cyclohexene from cyclohexanol is to distil the latter in the presence of about 3-4 percent of concentrated sulfuric acid. The temperature is 140-145°, and the yield is 89 percent. This is a rather remarkable catalytic effect.

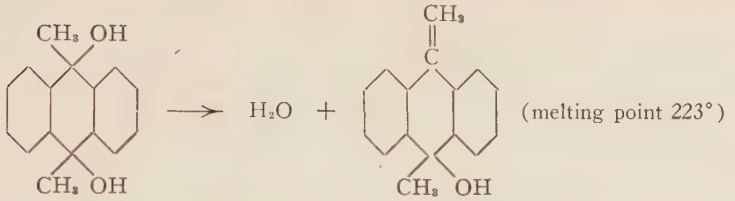
One of the products of the pyrogenic decomposition of cyclohexanol [126] above 500° is butadiene. An example is listed in the patent specification wherein cyclohexanol is heated alone, whereas 2-methylcyclohexanol is heated in the presence of iron filings. In the latter case, a homolog of butadiene is formed. Although of scientific interest, this method has little commercial value at present.

With a heavier molecule, dimethyl-hydroxy-tetralin, the dehydration occurs easily [127] by heat alone, and from 2.6 grams there is formed 2 grams of the unsaturated hydrocarbon at 200°.



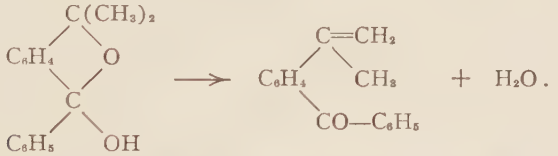
9,10-Dimethylanthracene-diol melts at 181°, and loses water [128] fairly readily. If it is kept at 70° for several days, the reaction proceeds [129] as follows:

[125] Senderens, *Compt. rend.* 177, 1183 (1923).
[126] Brit. 27,555, 1910; Schotz, "Synthetic Rubber," New York, D. Van Nostrand Co., 1926, p. 44.
[127] Schroeter and others, *Ber.* 51, 1603 (1918).
[128] Guyot and Staehling, *Bull. soc. chim.* 33, 1144 (1905).
[129] Dunlay, private communication.

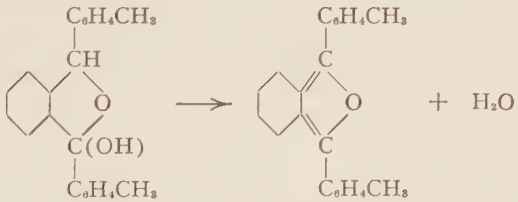


The same reaction may be induced in boiling acetic acid solution. As would be expected, 9,10-diphenylanthracene-diol is more stable.[130] Furthermore, its decomposition cannot follow a simple mechanism, since the product of the reaction (by heating in paraffin oil at 250-300°, or by heating in a solution of nitrobenzene, or by heating just above the melting point, 263° (or 247°)) is 9,10-diphenylanthracene.

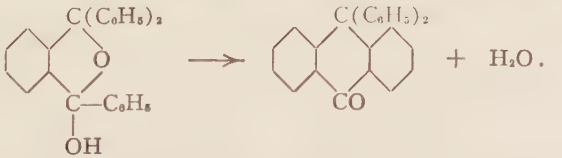
Three hydroxyphthalans all behave differently when heated. Thus, dimethyl-phenyl-hydroxyphthalan[131] yields *o-iso*propenyl benzophenone by distillation at atmospheric pressure:



Ditolyl-β,β-benzofurane[132] is very easily formed at 90° from the corresponding ditolyl-hydroxyphthalan:



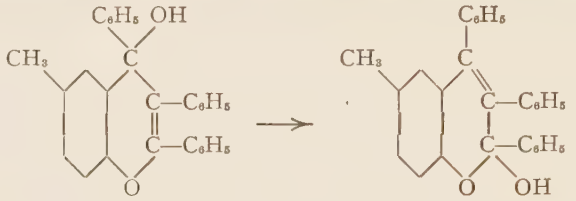
Finally, triphenyl-hydroxyphthalan[133] may be dehydrated at 300° in a vacuum into a compound which is most probably diphenyl-anthrone:



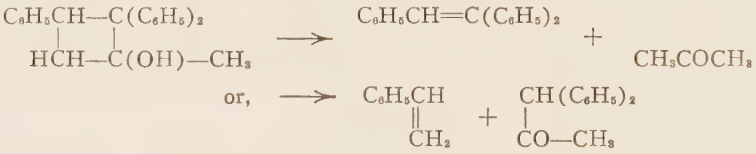
[130] Howell and Dunlay, unpublished results; Dunlay, private communication. *Also* Haller and Guyot, *Bull. soc. chim.* **31**, 795 (1904).
[131] Barnett, Cook and Nixon, *J. Chem. Soc.* **1927**, 504.
[132] Guyot and Vallette, *Ann. chim.* [8] **23**, 388 (1911).
[133] Shibata, *J. Chem. Soc.* **95**, 1449 (1909); Hewitt and Steinberg, *Proc. Chem. Soc.* **28**, 140 (1912); Howell, *J. Am. Chem. Soc.* **42**, 2333 (1920).

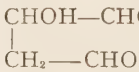
The structure for the compound formed as proposed by Shibata was quite different; it involved the peculiarity of a 3-membered ring and a 6-membered ring (aromatic) with one side in common, and such a structure is without a precedent in the literature.

The rearrangement of 2,3,4-triphenyl-6-methylchromen-4-ol (melting point 140°) into the -2-ol isomer takes place [134] either by heating above the melting point, or by heating for one hour on the steam bath:



Distillation of 1-methyl-2,2,3-triphenyl-cyclobutanol [135] at ordinary pressure causes two types of ring scission:



Quercitol,[136]  , loses water at 240° in a vacuum, and hydroquinone, quinone and pyrogallol are formed. In contrast, the hexahydroxy analog, inositol, boils undecomposed in a vacuum at 319°, as does *l*-inositol at about 200°. The following transformation [137] proceeds on distillation:

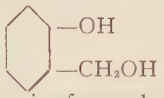
Phenols.

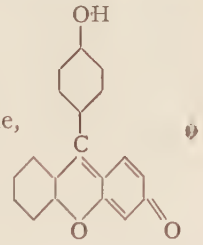
Phenol is extremely resistant to heat. Even by prolonged exposure [138] to red heat, only a small quantity of decomposition products result. Among these products of decomposition may be identified benzene and *p*-hydroxy-diphenyl. According to Kramers,[139] the pyrogenic products at a red-yellow heat are benzene, toluene, naphthalene, anthra-

[134] Ziegler, Fries and Sälzer, *Ann.* **448**, 249 (1926).
[135] Staudinger and Rheiner, *Helv. Chim. Acta*, **7**, 8 (1924).
[136] Prunier, *Ann. chim.* [5] **15**, 1 (1878).
[137] Eykman, *Ber.* **24**, 1278 (1891).
[138] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).
[139] Kramers, *Ann.* **189**, 129 (1877).

cene and carbon. This work is open to criticism, as Fischer and Schrader [140] point out, because of the influence of hydrogen on the thermal decomposition of aromatics. Thus, at the elevated temperature of the reaction, hydrogen causes dealkylation of alkyl benzenes, and dehydroxylation of phenols. They also criticize the work of Müller, who stated [141] that phenol decomposes at 700-800° chiefly into one mol of carbon monoxide, three of hydrogen and five of carbon, although benzene, ethylene, methane and tars are also formed. Phenol appears [142] to be 98 percent decomposed at 930°, but even at this very high temperature, some escapes and may be positively identified. In their work, a solution of 5 grams of phenol in 500 cc. of water was decomposed during 4.5 hours.

m-Cresol, diluted with 3.5-8 times the amount of hydrogen,[143] is reduced to benzene in 95-98 percent yields in a tinned-iron tube at 720-730°. Lignite creosote gives only 58 percent of its weight of benzene. The elimination of the methyl group in *m*-cresol is not prevented by using a mixture of hydrogen and methane, or by using carbon monoxide without hydrogen. In the latter case, a 45 percent yield of benzene appears, but no toluene.

When saligenin,  , is heated [144] above 100°, at first a fusible saliretin resin is formed, accompanied by the elimination of water. With more heat, an infusible resin results. It is interesting to compare this reaction with that for the manufacture of Bakelite, in which phenol and formaldehyde are heated under pressure, together with a little ammonia.

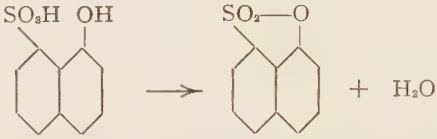
Phenol is liberated [145] from *p*-hydroxyphenyl fluorone, 

at the melting point, 285-295°.

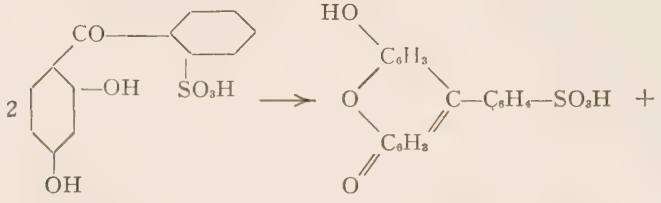
1,8-Naphtholsulfonic acid is easily converted [146] into naphthosulton

[140] Fischer and Schrader, *Brennstoff Chem.* **1**, 22 (1920); *Chem. Abstracts* **15**, 590 (1921).
[141] Müller, *J. prakt. Chem.* **58**, 1 (1898).
[142] Meyer and Wesche, *Ber.* **50**, 441 (1917).
[143] Fischer, Schrader and Zerber, *Ges. Abhandl. Kennt. Kohle* **6**, 128 (1921); *Chem. Abstracts* **18**, 2799 (1924).
[144] Piria, *Ann.* **56**, 41 (1845); de Laire, D.R.P. 189,262; *Chem. Zentr.* **1907**, II, 2002.
[145] Gomberg and Snow, *J. Am. Chem. Soc.* **47**, 208 (1925).
[146] Schultz, *Ber.* **20**, 3162 (1887).

by heating at atmospheric pressure; naphthosulton boils without decomposition.

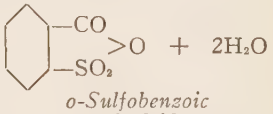


The preparation of sulfonefluorescein,[147] evidently in fairly good yields, is accomplished by heating 2,4-dihydroxybenzoyl-benzene-*o*-sulfonic acid at 160-170° for two hours.



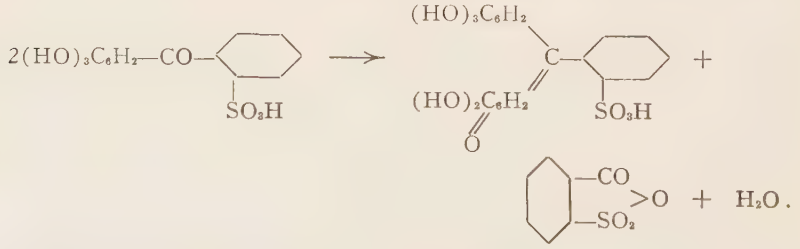
2,4-Dihydroxybenzoyl-benzene-o-sulfonic acid

Sulfonefluorescein



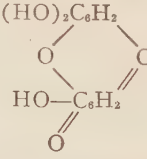
o-Sulfobenzoic anhydride

It was not stated whether resorcinol was thought to be an intermediate product, but work was described showing that sulfonefluorescein ($+ 2H_2O$) may be formed when the dihydroxy acid is heated for 4 hours at 160-170° with resorcinol. Since the yields were omitted by the authors, no deductions may be made inasmuch as the temperature was the same, and the time twice as long, as the experiment in which resorcinol was omitted. The course of pyrolysis[148] of 2,3,4-trihydroxybenzoyl-benzene-*o*-sulfonic acid is similar, except that pyrogallol sulfonephthalein (2 grams from 5 grams) may be isolated as an intermediate product by heating the acid for 6 hours at 140°. Thus:

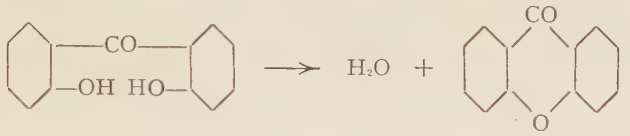


[147] Orndorff and Vose, *J. Am. Chem. Soc.* **46**, 1901 (1924).
[148] Orndorff and Fuchs, *J. Am. Chem. Soc.* **48**, 1939 (1926).

At 200°, pyrogallol sulfonephthalein loses a molecule of water and changes into sulfonegallein,

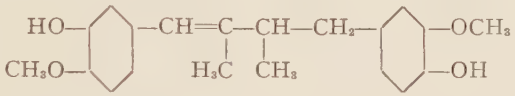


A partial conversion of *o,o'*-dihydroxybenzophenone [149] is effected by distillation:

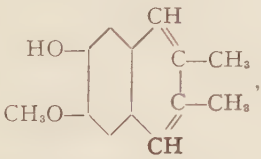


and the conversion of *o,o'*-dihydroxy-diphenylmethane to xanthene is spontaneous.

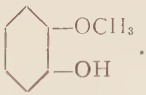
Guaiacum resinic acid [150] has the probable formula,



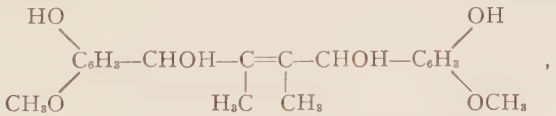
Distillation of this substance [151] gives, among other products, pyroguaiacin,



and guaiacol,



. Two hydrogen atoms are unaccounted for. Both pyroguaiacin and guaiacol are also formed during the dry distillation [152] of *iso*lariciresinol,



and in addition, carbon dioxide, gaseous hydrocarbons, and an aqueous layer. A compound, having the melting point of 140°, is also formed. If *iso*lariciresinol decomposed in the manner of other alcohols (pp. 164 and 175) which possess unsaturation *α* to the carbinol group, then vanillin and butene, or guaiacol and dimethyl maleic aldehyde would be reasonable products to expect. It may be pointed out that the phenolic group plays little or no part in these transformations.

[149] Richter, *J. prakt. Chem.* [2] **28**, 284 (1883); Graebe and Feer, *Ber.* **19**, 2609 (1886).
[150] Schroeter and others, *Ber.* **51**, 1592 (1918).
[151] Herzig and Schiff, *Monatsh.* **18**, 714 (1897).
[152] Bamberger and Vischner, *Monatsh.* **21**, 564 (1900).

Metallic Derivatives of Alcohols.

When methanol is heated at 200° with sodium methylate [153] there is no reaction, but at 230-240° the decomposition is complete. At 300°, sodium methylate [154] gives the following reaction, almost quantitatively:

$$6CH_3ONa \longrightarrow 9H_2 + Na_2C_2 + 2Na_2CO_3 + 2C.$$

Potassium methylate behaves similarly, but gives free potassium and not potassium carbide. This statement seems very interesting and unusual. Barium methylate breaks down at 350°:

$$2(CH_3O)_2Ba \longrightarrow 6H_2 + BaO + BaCO_3 + 3C.$$

Sodium ethylate, according to Durand, pyrolyzes either into ethylene and sodium hydroxide or into carbon, hydrogen and sodium hydroxide. The hydroxide thus formed may catalyze the decomposition of ethylene, but Fry [155] could find no evidence to indicate that ethylene reacts with fused caustic alkalies. Both Guerbet and Nef [156] also found ethylene and hydrogen. Guerbet heated sodium ethylate for a long period in the presence of alcohol and found sodium acetate, whereas Nef heated sodium ethylate alone at 300° and reported sodium carbonate. From 17.5 grams of the alcoholate, Nef found 0.9 gram of carbon, a 48.6 percent yield of ethylene (estimated from 23.5 grams of ethylene bromide), and 3.65 liters of a gas "which behaved like hydrogen". Fry's results would lead to the following interpretation of this reaction.

$$CH_3CH_2ONa \longrightarrow CH_2{=}CH_2 + NaOH,$$

and

$$CH_3CH_2ONa + 2NaOH \longrightarrow CH_3{-}C(ONa)_3 + 2H_2$$

In the event of sodium carbonate formation, methane should have been noticed as well, due to the well-known thermal reaction of sodium acetate and sodium hydroxide. Another investigator, de Coninck, also studied [157] this reaction, and observed ethylene, acetylene and hydrogen as the gaseous products from the heating of sodium ethylate.

Sodium *iso*propylate also gives carbon, hydrogen and the olefine, propylene, at 250-290° (see Nef, reference 156). From 0.244 mol, there was formed 0.166 mol of carbon, 0.223 mol of hydrogen (of uncertain purity), and 0.057 mol of propylene. In comparison, 0.26 mol of sodium ethylate gave 0.075 mol of carbon, 0.16 mol of hydrogen, and 0.124 mol of ethylene.

[153] Guerbet, *Bull. soc. chim.* [3] **27**, 584 (1902).
[154] Durand, *Compt. rend.* **172**, 1504 (1921); Nef, *Ann.* **318**, 196 (1901).
[155] Fry, Schulze and Weitkamp, *J. Am. Chem. Soc.* **46**, 2271 (1924).
[156] Guerbet, *Compt. rend.* **128**, 1002 (1899). Nef, *Ann.* **318**, 177 (1901).
[157] de Coninck and Chauvenet, *Bull. acad. roy. Belg. cl. sci.* **1907**, 33. *Chem. Abstracts* **1**, 1969 (1907).

A considerable portion of sodium *iso*butylate is unaffected in 2.5 hours at 280-360°. However, small amounts of *iso*butyraldehyde, sodium *iso*butyrate, octyl glycol and olefines are formed. The olefine bromides boil from 130-150°, but butylene bromide predominates. At 270-280°, *sodium* iso*amylate* liberates a 36.8 percent yield of trimethylethylene (not *iso*propyl-ethylene), with only small amounts of other olefines.[158] A considerable amount of hydrogen (probably), and some carbon are also produced, but no trace of *iso*valeric acid. *Sodium tertiary-amylate* is only gradually pyrolyzed at 300-350°.

When these sodium alcoholates are heated with soda-lime, there is a large conversion into the salt of the corresponding acid, and a correspondingly large evolution of hydrogen. This, however, is exactly what one would expect.

Mono-sodium glycerate, $CH_2OH—CHOH—CH_2ONa$, is much less stable[159] to heat than is glycerol. Hydrogen is evolved at 260° (90-98 percent purity), and the gas is entirely free from olefines. Sixteen liters of this gas is produced from 150 grams of material. The chief product of the reaction is racemic lactic acid, but methanol and propionic acid (salt) are also formed. In addition, there are smaller amounts of formates, oxalates and carbonates. The reaction produced no propylene glycol, but this substance is produced in good yields if molecular proportions of sodium hydroxide and glycerol are heated together. It is entirely possible that the hydrogen formed (above) is the result of the action of the liberated alkali.

Aluminum methylate is rather stable; it may be distilled *in vacuo*.[160] Aluminum ethylate may also be distilled in a vacuum, but at ordinary pressure it is completely decomposed into aluminum oxide, ethylene and alcohol. Aluminum amylate behaves similarly.

Sabatier's viewpoint[161] regarding the function of a catalyst, such as alumina or thoria, is stimulating even though it is not all-inclusive. It is mentioned here, since he postulates an intermediate transitory reaction product which is at once decomposed at the temperature of the reaction, thereby restoring the catalyst. With alcohols, for example, the following steps are assumed:

$$2ROH + Al_2O_3 \longrightarrow H_2O + Al_2O_2(OR)_2$$

$$Al_2O_2(OR)_2 + ROH \longrightarrow 2R_2O + Al_2O_3 + H_2O$$

or

$$Al_2O_2(OC_nH_{2n+1})_2 \longrightarrow C_nH_{2n} + Al_2O_2(OH)_2.$$

[158] *See also* Lachman, *J. Am. Chem. Soc.* **45**, 2359 (1923).
[159] Nef, *Ann.* **335**, 281-285 (1904).
[160] Gladstone and Tribe, *Chem. News* **42**, 267 (1880); **44**, 257 (1881).
[161] Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co., 1922, paragraphs 169, 626, 731, 763, 790, 809, 859, 878.

Similarly, with mercaptans:

$$2RSH + CdS \longrightarrow H_2S + (RS)_2Cd$$
$$(RS)_2Cd \longrightarrow R_2S + CdS,$$

or at higher temperatures,

$$(RS)_2Cd \longrightarrow H_2S + CdS + 2(\text{olefines}).$$

Or, with alkyl halides to olefines, by means of barium chloride:

$$RCl + BaCl_2 \xrightarrow{260\text{-}300^\circ} HCl + C_nH_{2n}\begin{matrix}<\text{BaCl}\\ \quad\downarrow\ \ \text{Cl}\end{matrix}$$
$$C_nH_{2n} + BaCl_2.$$

Reactions, such as esterifications over heated metallic oxides, or the conversion of alcohols to amines over thoria at 300-350°, are explained on a similar basis.

Magnesium Compounds.

Grignard Reaction.

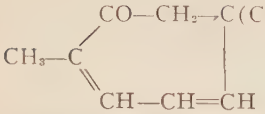
The Grignard reaction is a well-known way to prepare tertiary alcohols. Prior to hydrolysis, the magnesium compound may be represented by the general formula $RCH_2—CR_2—OMgX$. It is remarkably easy for such compounds to form olefines, $RCH=CR_2$, with the elimination of HO—MgX. Thus, phenyl-2-propene-1 may be formed [162] by heating the Grignard reagent, $C_6H_5—C(CH_3)_2—OMgI$, in the presence of the original ether for 6 hours on a water bath. Again, the intermediate

$$C_6H_5—\underset{\displaystyle CH_3}{\overset{\displaystyle C_{10}H_7}{\overset{|}{\underset{|}{C}}}}—O—MgBr$$

, which may be formed either [163] from methyl magnesium bromide and phenyl α-naphthyl ketone, or [164] from α-naphthyl magnesium bromide and acetophenone, ultimately, by refluxing in ether, yields only the olefine, $Ar_2C=CH_2$, and none of the tertiary alcohol. To isolate the olefine, the ethereal solution was treated with dilute sulfuric acid and the ether layer withdrawn, dried and distilled. Similarly, heating [165] methyl *iso*butyl ketone and propyl magnesium iodide for two hours on the steam bath, followed by treatment with ice water and dilute hydrochloric acid, gives the olefine, methyl-4-propyl-2-pentene-1.

[162] Klages, *Ber.* **35**, 2647 (1902).
[163] Acree, *Ber.* **37**, 2753 (1904).
[164] Stoermer and Simon, *ibid.* **37**, 4163 (1904).
[165] Clarke and Beggs, *J. Am. Chem. Soc.* **34**, 61 (1912).

With cyclic ketones, the same holds true. Thus, eucarvone,[166]



, after routine treatment with methyl magnesium iodide, gives tetramethyl-cycloheptatriene. A 70 percent yield of α-phenyl indene together with some benzene and diphenyl, comes from the interaction[167] of phenyl magnesium bromide and α-hydrindone, $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH_2$. If ethyl magnesium bromide is used instead, the tertiary alcohol may actually be isolated. However, by distillation at atmospheric pressure, it also is dehydrated into α-ethyl indene. Grignard syntheses[168] using cyclohexylidene-cyclohexanone may give both the anticipated tertiary alcohol or the unsaturated compounds. With cyclohexanone and naphthyl magnesium bromide,[169] apparently only the unsaturated compound, naphthyl-cyclohexene, results.

Magnesium Pinacolate.

Attempts to prepare dimethyl butadiene[170] by the dry distillation of magnesium pinacolate, $((CH_3)_2C(O)-)_2Mg$, were unsuccessful. Instead, the products of the reaction are benzene, mesityl oxide, and an unidentified mixture of compounds, some of which are unsaturated.

Metallic Derivatives of Phenols.

Sodium phenoxide[171] turns brown at 400°, with but little decomposition at lower temperatures. Vigorous ebullition sets in at 485°, and from 500 grams there may be collected 20 liters of gas which is 90-91 percent hydrogen, 7-8 percent methane or ethane, 1.4 percent oxygen and 0.5 percent ethylene. The distillate, amounting to 5-8 percent, is about four-fifths benzene, admixed with lesser quantities of diphenyl, diphenyl ether, and hydroxydiphenyl. About 100 grams of phenol, from unchanged sodium phenoxide, may be recovered by hydrolyzing the residue. About 100 grams also of *o,o'*-dihydroxy-diphenyl may be obtained in this process, as well as small amounts of other isomeric dihydroxydiphenyls and of *o*-hydroxydiphenyl. According to Durand,[172]

[166] Rupe and Kerkovius, *Ber.* **44**, 2702 (1911).
[167] von Braun, *Ber.* **50**, 1661 (1917).
[168] Garland and Reid, *J. Am. Chem. Soc.* **47**, 2337 (1925).
[169] Weiss and Woidich, *Monatsh.* **46**, 453 (1926).
[170] Calvert, *India Rubber Rev.* **26**, 48 (1926); *Chem. Abstracts* **20**, 3685 (1926).
[171] Hofmann and Heyn, *Brennstoff Chem.* **2**, 147 (1921); *Chem. Abstracts* **15**, 3099 (1921); **16**, 75 (1922).
[172] Durand, *Compt. rend.* **172**, 1504 (1921).

sodium phenoxide pyrolyzes into hydrogen, carbon and sodium hydroxide.

More methane is produced [173] from sodium *p*-tolyl oxide (or the meta isomer) at 450-600° than from sodium phenoxide. Much cresol is present in the liquid products of the reaction. At 450°, *lithium phenoxide* breaks down into liquid products, and hydrogen, methane, carbon monoxide and carbon dioxide. Basic calcium phenoxide, HO—Ca—OC_6H_5, behaves analogously except that no carbon dioxide is in the products of reaction. If the latter reaction (at 450°) is conducted in a stream of carbon dioxide, the reaction proceeds completely to phenol and calcium carbonate. Fischer and Ehrhardt noted phenol as the chief product of the pyrogenic decomposition of calcium phenoxide, $Ca(OC_6H_5)_2$, but Niederhausern [174] had previously demonstrated the formation of diphenyl ether and of diphenylene oxide. Below red heat, aluminum phenylate [175] gives hydrogen, methane and liquid products which contain benzene, phenol, diphenyl ether and xanthene.

Gladstone and Tribe [175] found that a 30-35 percent yield of diphenyl ether is obtainable by subjecting aluminum phenoxide, $Al(OC_6H_5)_3$, to dry distillation. This was the first technical synthetic method for this ether. Its use in perfumes, due to its geranium-like odor, is well known. The more modern method of synthesis [176] is to pass phenol vapors over thoria at 450°. Some diphenylene oxide is also formed.

In Gladstone and Tribe's work, there was an unidentified compound, $C_{13}H_{10}O$, which Möhlau [177] proved to be xanthene. Dry distillation to 200° was found to give chiefly phenol, but above that temperature a viscid liquid was collected, hydrogen and methane were evolved, and there remained a residue of carbon and alumina. Fractionation of 273 grams of the viscid liquid gave the results shown in Table XXII.

TABLE XXII. *Composition of Liquid Fraction Resulting from Distillation of Xanthene.*

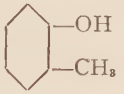
Weight of Fraction (Grams)	Boiling Range °C.	Composition
2.3	to 130	Water and benzene.
96	130-200	Almost entirely phenol.
26	200-250	Largely phenol, but some diphenyl ether.
110.5	250-300	Largely diphenyl ether, but some xanthene.
14	300-350	Xanthene, and (phenyl xanthene?).
2	above 350	

[173] Fischer and Ehrhardt, *Ges. Abhandl. Kennt. Kohle* **4**, 237 (1919); *Chem. Abstracts* **15**, 3635 (1921).
[174] Niederhausern, *Ber.* **15**, 1120 (1882).
[175] Gladstone and Tribe, *J. Chem. Soc.* **41**, 5 (1882). *Chem. News*, **44**, 257 (1882).
[176] Sabatier and Mailhe, *Bull. soc. chim.* [4], **11**, 843 (1912).
[177] Möhlau, *Ber.* **49**, 168 (1916).

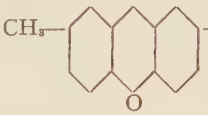
Möhlau suggested the following equation:

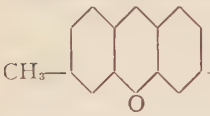
$$2Al_3(OC_6H_5)_9 \longrightarrow 2Al_2O_3 + 10C + H_2 + CH_4 + C_6H_6 + 3C_6H_5OH + 2(C_6H_5)_2O + C_6H_4\!<\!\overset{CH_2}{O}\!>\!C_6H_4,$$

and considered that xanthene formation was best interpreted as due to the reaction:

$$CH_4 + C_6H_5OH \longrightarrow H_2 + \text{  }$$

followed by a further condensation of phenol with the *o*-cresol, thereby giving xanthene, hydrogen and water.

Dry distillation of aluminum *p*-cresylate, according to Gladstone and Tribe, gives a much smaller yield of the ether but a correspondingly larger amount of the substance, $C_{15}H_{14}O$, which is undoubtedly 2,8-dimethyl-xanthene,  . Aluminum

thymolate produces an isomer, presumably 3,7-dimethyl-xanthene,  , with the simultaneous evolution of propylene.

From aluminum *o*-cresylate may be obtained the other isomer, 4,6-dimethyl-xanthene.

Gladstone and Tribe found that aluminum β-naphthylate pyrolyzes chiefly into β-naphthyl ether:

$$(C_{10}H_7O)_6Al_2 \longrightarrow Al_2O_3 + 3(C_{10}H_7)_2O,$$

whereas the α-naphthylate gives a hydrocarbon, apparently β,β-dinaphthyl.

CHAPTER 8.

ETHERS.

The pyrolytic reactions of ethers may be conveniently discussed under four headings:

(1) Aliphatic ethers, R—CH_2—O—CH_2—R, etc., from which aldehydes and hydrocarbons are formed.
(2) Aromatic ethers, Ar—O—R, or Ar—O—Ar, from which phenols are produced.
(3) Unsaturated ethers, which rearrange on heating. Especially these possess the vinyl type of unsaturation or the allyl type of unsaturation.
(4) Complex ethers, from which alcohols are frequently eliminated by heat.

Aliphatic Ethers.

Between 555-771°, the pyrolysis of *dimethyl ether*[1] is empirically unimolecular at pressures above 300 mm., but at lower pressures it is no longer unimolecular. The reaction gives methane, hydrogen and carbon monoxide:

$$CH_3OCH_3 \longrightarrow CH_4 + [HCHO] \longrightarrow CH_4 + H_2 + CO.$$

The principal change in the decomposition of diethyl ether is to acetaldehyde and ethane:

$$C_2H_5—O—C_2H_5 \longrightarrow CH_3CHO + C_2H_6.$$

To be sure, Berthelot demonstrated[2] that considerable acetylene might be realized from ether at red heat, but acetylene is formed as the result of secondary changes. When ether is passed through a short platinum tube[3] at 1150° at a rate of 4.86 grams per minute, more than 35 percent of the condensate is acetaldehyde and the remainder is mostly unchanged ether. However, some crotonaldehyde is also present. The gaseous mixture contains not only ethane, but its decomposition products (p. 54) ethylene, acetylene and hydrogen; also it contains methane and carbon monoxide, formed from the acetaldehyde. There may be some evidence

[1] Hinshelwood and Askey, *Proc. Roy. Soc.* (London) **115A**, 215 (1927).
[2] Berthelot, *Ann. chim phys.* [3] **67**, 52 (1863).
[3] Peytral, *Bull. soc. chim.* **35**, 964 (1924).

for an unimportant secondary reaction of diethyl ether into two molecules of ethylene and one of water.

Ether appears to be fairly stable [4] below 500°, but at 550° pyrolysis sets in rather vigorously and acetaldehyde is formed in large amounts. Disregarding the acetaldehyde and carbon dioxide, which Nef removed by an alkaline wash, there is formed 17.5 percent of the theoretical amount of ethylene and 13.5 liters of other gases formed from 20 grams of absolute ether, applied during 2¼ hours at 590-610°. The analysis of the gases follows: methane 36.56 percent, carbon monoxide 30.5 percent, ethane 16.24 percent, and hydrogen 16.7 percent. By measuring the change in total pressure [5] when ether is heated in silica bulbs at 525, 555 or 588°, Hinshelwood has found that the reaction at high pressures is unimolecular, but at low pressures is nearly bimolecular. The reaction is homogeneous, and is not influenced by the walls of the bulbs. The velocity of the reaction may be represented by the equation:

$$K = 26.47 - 53{,}000/RT .$$

Carbon dioxide is not formed, but an analysis of the gases formed at 477° and 587° respectively gives carbon monoxide, 27.9 and 28.7 percent; methane, 54.4 and 55.3 percent; ethane, 8.8 and 8.2 percent; ethylene, 8.9 and 7.8 percent. Rather curiously, it has been found that hydrogen may completely stop the falling-off of the unimolecular law at low pressures. This indicates that collisions with hydrogen molecules can maintain the supply of activated ether molecules as effectively as collisions with other ether molecules. Helium or nitrogen, as diluents, have no influence.

The pyrolysis of an aliphatic ether to an aldehyde is quite general, but if one or both of the groups which is attached to the oxygen in the ether is aromatic this never occurs. *Dibenzyl ether* is aliphatic, and essentially is converted by heat into toluene and benzaldehyde:

$$C_6H_5CH_2OCH_2C_6H_5 \longrightarrow C_6H_5CHO + C_6H_5CH_3 .$$

This reaction was first studied by Cannizzaro,[6] and later by Lowe,[7] who gave 295-298° as the decomposition point. Lachman showed that the decomposition occurs at 210-215°, although at a slow rate.[8] Thirty grams of the ether, if heated in a sealed tube at this temperature for 5 days, gives 8.5 grams of toluene, 7.5 grams of benzaldehyde, 8 grams of unchanged ether, and 5.5 grams of an oil, most of which boils at

[4] Nef, *Ann.* **318**, 198 (1901).
[5] Hinshelwood, *Proc. Roy. Soc.* (London) **114A**, 84 (1927).
[6] Cannizzaro, *Ann.* **92**, 113 (1854).
[7] Lowe, *Ann.* **241**, 374 (1887); *see also* Oddo, *Gazz. chim. ital.* **31**, I, 367 (1901).
[8] Lachman, *J. Am. Chem. Soc.* **45**, 2358 (1923).

217° at 5 mm. No gaseous products are formed in this pyrolysis, nor does water appear to be formed.

If dibenzohydryl ether is subjected[9] to very gradual distillation (5 grams in 15 min.), the distillate (boiling point 270-295°) is almost exclusively benzophenone and diphenyl methane:

$$(C_6H_5)_2CH{-}O{-}CH(C_6H_5)_2 \longrightarrow (C_6H_5)_2CO + (C_6H_5)_2CH_2.$$

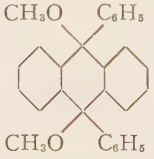
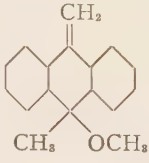
A little tetraphenyl ethane and resinous matter remains in the flask. With more rapid distillation some of the ether distils without change. If, instead of distilling the ether, it is refluxed for 8.5 hours (300°), the products from 20 grams of the ether are as follows: 4.2 grams of benzophenone, 3 grams of diphenyl methane, no tetraphenyl-ethylene, and 6.8 grams of tetraphenyl-ethane. A similar process occurs in a sealed tube at 350°. It will be recalled that these results are almost the counterpart of those obtained from benzohydrol (p. 160).

Again, with alkyl triphenylmethyl ethers,[10] decomposition into an aldehyde (or ketone) is general. The yields, in each of the three cases illustrated below, are excellent.

$$(C_6H_5)_3C{-}O{-}CH_2CH_3 \xrightarrow{\text{above } 300^\circ} (C_6H_5)_3CH + CH_3CHO$$

$$(C_6H_5)_3C{-}O{-}CH(CH_3)_2 \xrightarrow{270^\circ} (C_6H_5)_3CH + (CH_3)_2CO$$

$$(C_6H_5)_3C{-}O{-}CH_2CH_2CH_2CH_3 \longrightarrow (C_6H_5)_3CH + n{-}C_3H_7{-}CHO$$

Formaldehyde is vigorously evolved when the dimethyl ether of 9,10-diphenyl-anthracene-diol,  , is heated[11] above 300°. Presumably, there is either a simultaneous elimination of methanol or of hydrogen, for 9,10-diphenylanthracene is the residual product. Similarly, the dibenzyl ether liberates benzaldehyde. The dimethyl ether of 9,10-dimethyl-anthracene-diol[12] loses a molecule of methanol at 100° in a vacuum, giving the substance,  .

[9] Nef, *Ann.* 298, 234 (1897).
[10] Norris and Young, *J. Am. Chem. Soc.* 46, 2582 (1924); *see also*, this monograph, p. 36.
[11] Dunlay, private communication.
[12] Guyot and Staehling, *Bull. soc. chim.* 33, 1144 (1905).

Iodo-dimethyl ether, $CH_3—O—CH_2I$, boils[13] for the most part without decomposition at 122-125°, but it changes gradually on standing into methyl iodide and a polymer of formaldehyde.

A study of glycid ethyl ether, $CH_2—CH—CH_2—O—C_2H_5$ (epoxide ring), at 450° over pumice[14] (37.1 grams during 6 hours) gives 5.5 liters of gases and 28 cc. of condensate which contains much of the original ether and some acetaldehyde. In addition, 9 grams of it boils at 120-140° and is the ethyl ether of acetol, $CH_3COCH_2—O—C_2H_5$, an isomer of the original ether. Five grams, boiling point (23 mm.) 80-85°, was considered to be glycerol diethyl ether, $C_2H_5O—CH_2—CHOH—CH_2OC_2H_5$.

Although heterocyclic nuclei are present in hydrobenzoin anhydride and *iso*hydrobenzoin anhydride, these compounds are essentially ethers. Both have the formula, $C_6H_5CH—O—CHC_6H_5$ / $C_6H_5CH—O—CHC_6H_5$, and neither is convertible into the other by heat. Both undergo pyrolysis[15] into benzaldehyde and stilbene, without the formation of gaseous products, when maintained in a sealed tube for 8 hours at 250-270°.

Aromatic Ethers.

The property of aldehyde formation, which was so characteristic with the aliphatic ethers, seems to be entirely dormant when one of the groups attached to the oxygen atom is aromatic. Phenols are formed instead. The answer for the difference undoubtedly involves the relative electronegativities of the two radicals in question. Aryl radicals are more negative than alkyl, which means that they are more firmly attached to their valence electrons; therefore, they cling to the oxygen atom in preference to the option of allowing scission at that point.

To illustrate this point, *anisole*[16] undergoes pyrolysis at 380-400° into phenol, but no trace of trioxymethylene. In this case, the reaction is exclusively:

$$2C_6H_5OCH_3 \longrightarrow 2C_6H_5OH + C_2H_4.$$

The same is true (Bamberger) of phenetole, of β-naphthyl ethyl ether (310-320° for 24 hours), of phenyl *iso*butyl ether (380-400°), and of the ethyl ether of thymol (360-400°, but only a trivial pyrolysis at 320-330°). In each case, either phenol or β-naphthol or thymol may be identified together with the olefine.

[13] Henry, *Bull. acad. roy. Belg.* [3] **25**, 439 (1893).
[14] Nef, *Ann.* **335**, 240 (1904).
[15] Breuer and Zincke, *Ann.* **198**, 163 (1879).
[16] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917). Bamberger, *Ber.* **19**, 1818 (1896).

Recently it has been shown [17] that cyclohexyl phenyl ether gives phenol and cyclohexene by heating the ether in sealed tubes. Because of the reaction of phenol and cyclohexene to form *o*-cyclohexyl-phenol some of the latter is also always formed as well. It may be of interest to indicate the formation of *o*-cyclohexyl-*p*-cresol by heating *p*-cresol and cyclohexene.

Nearly a quantitative yield of phenoxybutyl-pyrrolidone [18] is reported in the following reaction, which takes place by gradual distillation:

$$(C_6H_5{-}O{-}(CH_2)_4)_2NH \longrightarrow C_6H_5OH + C_6H_5O{-}(CH_2)_4{-}N{=}(CH_2)_4.$$

The boiling point of phenyl benzyl ether drops rapidly [19] from 272° to 220° during 4 hours' refluxing. Much phenol is formed, and also toluene and unidentified material. With *p*-bromophenyl benzyl ether or the related compounds, $Br{-}C_6H_4{-}O{-}CH_2C_6H_4Br$ and 2,4—$Br_2C_6H_3{-}O{-}CH_2{-}C_6H_4Br$, hydrogen bromide is evolved by boiling; in general also, phenol or toluene or their substituted derivatives are also formed. The decomposition of the compounds is complete.

Diphenyl ether, or diphenyl oxide, is a remarkably stable compound and this fact has recently been utilized in the attempt to find a liquid of higher boiling point than water, which might be used in engines in the usual way except that the exhaust vapors, still very hot, should be carried over into the second boiler to generate steam for the second engine. This idea, which was first tried with mercury as the higher boiling liquid, has been successfully applied, so it is claimed, with diphenyl ether. Temperatures of 400-450° cause little or no deterioration of this substance. If, however, the vapors are passed through a glass tube at red heat, it breaks down [20] into phenol, benzene and diphenylene oxide:

$$2C_6H_5OC_6H_5 \longrightarrow (C_6H_4)_2O + C_6H_6 + C_6H_5OH.$$

In this case, it seems that the phenol and the benzene are both reduction products of the ether, caused by the liberation of hydrogen as diphenylene oxide is produced. The formation of diphenylene oxide in good yields was confirmed [21] by Meyer and Hofmann.

Baekeland and Bender [22] asserted that butaldehyde resin (from butyraldehyde, phenol and paraformaldehyde) possesses the structure of

[17] Skraup and Beifuss, *Ber.* **60**, 1070 (1927).
[18] von Braun, Blessing and Zobel, *Ber.* **57**, 187 (1924).
[19] Powell and Adams, *J. Am. Chem. Soc.* **42**, 657 (1920).
[20] Graebe and Ullmann, *Ber.* **29**, 1877 (1896).
[21] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[22] Baekeland and Bender, *Ind. Eng. Chem.* **17**, 230 (1925).

an ether, and showed that by heating it for an hour at 260°, it was largely converted into crystalline *p*-dihydroxy-diphenyl-butane:

$$CH_3CH_2CH_2—CH(C_6H_4OH)—O—C_6H_5 \longrightarrow CH_3CH_2CH_2CH(C_6H_4—OH)_2 \ (para).$$

Such a rearrangement is more typical of the allyl phenyl ethers than of the benzyl phenyl ethers. Possibly the mechanism is similar to that of phenyl cyclohexyl ether, which gave *o*-cyclohexyl-phenol on heating, but which was shown to proceed through the intermediate steps of phenol and cyclohexene. In the case in question, the intermediate products would then have been phenol and $CH_3CH_2CH{=}CH—C_6H_4OH$.

Unsaturated Ethers.

Vinyl Type with α,β-Unsaturation.

It has been pointed out that alcohols with α,β-unsaturation, namely, alcohols of the vinyl type, are extremely unstable and the only instances when enols may be isolated are when modifying groups, such as carbonyl, are adjacent. This is not the case with ethers, since ethyl vinyl ether, $C_2H_5—O—CH{=}CH_2$, and divinyl ether are isolable and fairly stable. It is interesting, however, to point out that the alkyl ethers of enols have frequently been shown to undergo rearrangement under the influence of heat into the keto isomers. Illustrative of this, ethyl α-phenyl-β-methoxy-acrylate rearranges[23] in 24 hours at 240° into ethyl phenylmethyl-formoacetate:

$$CH_3O—CH{=}C(C_6H_5)—CO_2C_2H_5 \longrightarrow H—\underset{\underset{O}{\|}}{C}—\underset{\underset{CH_3}{|}}{C}(C_6H_5)—CO_2C_2H_5.$$

Claisen[24] has prepared the *O*-ethyl ether of the enol form of acetophenone by the following reaction, which is induced by boiling at ordinary pressure:

$$C_6H_5—C(OC_2H_5)_2—CH_3 \longrightarrow C_6H_5—C(OC_2H_5){=}CH_2 \ (\text{b.p. } 209°) + C_2H_5OH$$

If, now, this enol ether is heated at two atmospheres for a few hours, there is formed *n*-propyl phenyl ketone:

$$C_6H_5\ \underset{\underset{OC_2H_5}{|}}{C}—CH_2 \longrightarrow C_6H_5—\underset{\underset{O}{\|}}{C}—CH_2—C_2H_5.$$

The *O*-methyl ether is prepared similarly, and it changes in like manner into propiophenone. *O*-Alkyl ethers of benzoyl acetone[25] have been

[23] Wislicenus and Schrötter, *Ann.* **424**, 215 (1921).
[24] Claisen, *Ber.* **29**, 2932 (1896).
[25] Weygand, *Ber.* **59**, 2253 (1926).

recently synthesized, but apparently they have not been studied from this point of view. Also, the *O*-ethyl ether of acetylacetone is known (boiling point (15 mm.) 72°, or 175-180° at 760 mm.), but attempts [26] to pyrolyze it seem not to have been undertaken. The compound, $(CH_3)_2C{=}C(OCH_3){-}COCH_3$, boils,[27] apparently without decomposition, at 167°.

Methoxy-β-methoxy-crotonic acid [28] has been heated with water in a sealed tube for 5 hours at 140-150°. Acetone and formaldehyde are the reported products, but the mechanism of the reaction is somewhat obscure. More than likely, the water does not play an inert rôle, and in part the effects may be hydrolytic ones. Had there been a migration, such as has been mentioned in the previous cases, the ketone would have been methylethyl ketone and not acetone. Thus, the hypothetical steps, which were not realized:

$$CH_3OCH_2{-}O{-}C(CH_3){=}CH{-}CO_2H \quad \text{into} \quad O{=}C(CH_3){-}CH(CH_2OCH_3){-}CO_2H \quad \text{into}$$

$$O{=}C(CH_3){-}CH_2{-}H + CO_2$$

$$H_3C + CH_2{-}H + HCHO$$

Acetone was definitely identified through its *p*-bromophenylhydrazone. If, instead of a protracted sealed tube reaction in the presence of water, the acid is distilled, it becomes partially esterified in the process. Possibly the mechanism is as follows:

$$R{-}O{-}C(CH_3){=}CH{-}CO_2H + R{-}O{-}C(CH_3){=}CH{-}CO_2H \longrightarrow$$

$$RO{-}C(CH_3){=}CH{-}CO_2R + [HO{-}C(CH_3){=}CH{-}CO_2H]$$

(let $R{=}CH_3{-}O{-}CH_2{-}$)

$$[HO{-}C(CH_3){=}CH{-}CO_2H] \rightarrow CH_3COCH_3 + CO_2$$

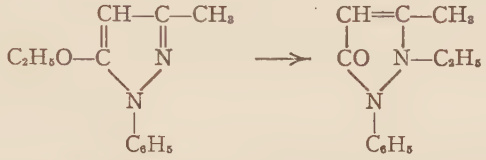
The yield of the ester is good. Carbon dioxide is evolved, and although acetone was not mentioned in this connection, it no doubt was also a product of this reaction. (See p. 350.)

After 12 hours in a sealed tube at 260-280°, phenyl vinyl ether,[29] $C_6H_5{-}O{-}CH{=}CH_2$, is still largely unchanged, but there is produced about a 20 percent yield of phenol, and 5 percent of a liquid "with a piercing odor". Phenyl acetaldehyde was not mentioned. *p*-Tolyl vinyl ether pyrolyzes more easily; even with two hours of refluxing at 180°,

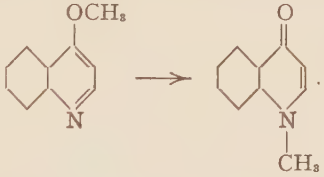
[26] Curtiss, *Am. Chem. J.* 17, 435 (1895).
[27] Pauly and Lieck, *Ber.* 33, 503 (1900).
[28] Simonsen and Storey, *J. Chem. Soc.* 95, 2106 (1909).
[29] Powell with Adams, *J. Am. Chem. Soc.* 42, 646 (1920).

there is considerable transformation into *p*-cresol and a high-boiling, alkali-insoluble product.

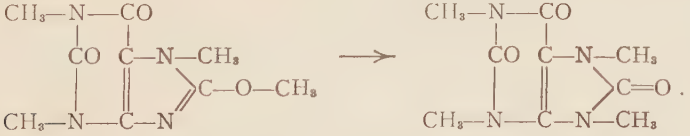
Many ethers of heterocyclic enols rearrange into the keto forms if heated. However, in these cases the alkyl group wanders to a nitrogen atom wherever it may be in preference to a β-unsaturated carbon. There is, for example, the rearrangement [30] of 1-phenyl-3-methyl-5-ethoxy-pyrazole into 1-phenyl-2-ethyl-3-methyl-pyrazolone-(5) by heating for 3 hours at 250°:



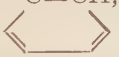
or the rearrangement,[31] at 300-310°, of 4-methoxy-quinoline (the methyl ether of kynurin) into *N*-methyl-γ-quinolone:



The complete transformation of trimethyl-cyanurate [32] into trimethyl *iso*cyanurate by refluxing (265°) is another case of the change of the *O*-enol ether into the keto isomer. The conversion of 8-methoxy (or 8-ethoxy)-caffeine [33] into tetramethyl uric acid is complete between 170-200°:



The cases that have been considered make it seem clear that there is some kind of attraction for the group *R* in R—O—C=C* to wander to the β-carbon which bears the asterisk. The phenyl ethers, R—O—C=CH, also possess this type of unsaturation, and the question



may be raised whether or not the same type of reaction should be ex-

[30] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Berlin and Leipzig, Walter de Gruyter Co., 2, 3, 376.
[31] Meyer, *Monatsh.* **27**, 255 (1906).
[32] Hofmann, *Ber.* **19**, 2064 (1886).
[33] Wislicenus and Körber, *Ber.* **35**, 1991 (1902).

pected in this case. With the simple ethers such as anisole and its homologs (see, e.g., p. 106), the answer appears to be in the negative. However, there are two features which tend to offset such a reaction. In the first place, the methyl group is fairly electronegative and is not readily detached from the valence bonds that tie it to oxygen. The obvious remedy is to find a more positive group, and the extreme case would be the selection of the allyl group (see pp. 38, 39). It is actually found that phenyl allyl ether rearranges very smoothly into *o*-allyl phenol:

This subject has been studied so exhaustively that it will be expounded in detail later. A second reason why anisole displays no tendency for this type of rearrangement may be because of the negative tendency for mono-phenols to assume the keto (quinone) structure. To be perfectly analogous, anisole should change in accordance with the equation:

Possibly the ethers of phloroglucinol might undergo this type of rearrangement because of the stability of derivatives of cyclohexanetrione-1,3,5. As yet, phloroglucinol derivatives have not been studied in this connection.

Imido Esters (Imino Ethers).

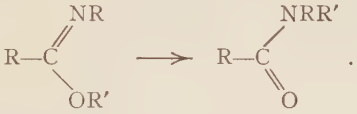
Imido esters are included here because the structures, R—O—C=C= and R—O—C=N—, are essentially similar. Imido esters fall into two groups regarding their behavior towards heat, namely, those with a substituted imino group and those with an unsubstituted imino group. Members of the former class undergo the same type of rearrangement that has already been treated with other α,β-unsaturated ethers. Imido esters of the latter class decompose characteristically into an alcohol and a nitrile or its polymer. These will be treated first.

Benzimido methyl ester, $C_6H_5—C(=NH)—OCH_3$, heated in a sealed tube [34]

[34] Wislicenus and Goldschmidt, *Ber.* **33**, 1467 (1900).

for 26 hours at 250-280°, gives crystals of cyaphenine, $(C_6H_5CN)_3$, when cooled to 0°. The main body of the filtrate consists of methanol and benzonitrile. Such decompositions proceed, in fact, even at ordinary temperatures, although at a slower rate. For example, Pinner [35] recommends as the best method of preparing cyaphenine that crude benzimido ethyl ester be allowed to undergo spontaneous decomposition at ordinary temperature. It has also been observed [36] that pure benzimido methyl ester decomposes completely in sealed tubes to cyaphenine after a number of years. No benzonitrile was found. In a parallel test, benzonitrile was found not to polymerize into cyaphenine. Benzimido ethyl and butyl esters were incompletely decomposed, and from each was isolated both benzonitrile and its polymer.

The presence of a group on the nitrogen seems essential to prevent this type of dissociation. It is characteristic of substituted imino ethers to rearrange into an amide:



This is the same type of reaction that has already been discussed with some ethers which possess α,β-unsaturation. Phenylformimino methyl ether (or *N*-phenyl-formimido methyl ester) is half recoverable [34] after 8 hours in a sealed tube at 240°. The yield of methyl formanilide is 40 percent.

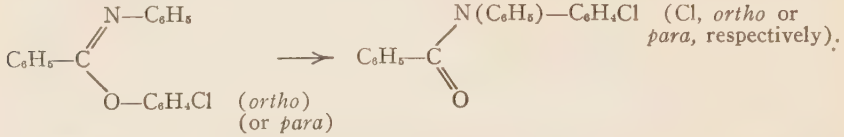
$$C_6H_5N{=}CH{-}OCH_3 \longrightarrow H{-}CO{-}N(CH_3){-}C_6H_5.$$

The ethyl ester is stated to pyrolyze similarly, giving a 65 percent yield; and *N*-phenyl-benzimido methyl ester, $C_6H_5{-}C(N{-}C_6H_5){-}OCH_3$, a 35 percent yield of methyl benzanilide (6 hours at 270-280°). These results, however, could not be duplicated by Lander,[37] who asserted that catalysts of some sort must be essential to the change. The best catalysts found were the alkyl iodides.

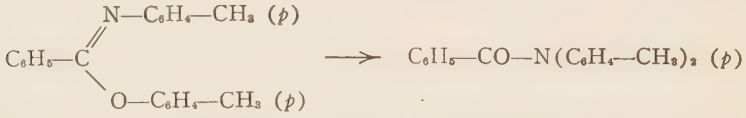
Phenyl groups have been shown to migrate by heat alone. Chapman's studies of iminoaryl ethers, in particular, is noteworthy. *N*-Phenyl-benzimido phenyl ester, $C_6H_5{-}C(OC_6H_5){=}NC_6H_5$, if maintained [38] for two hours at 270-300°, changes into diphenyl benzamide,

[35] Pinner, *Ber.* **22**, 1611 (1889).
[36] Johnson and Bass, *J. Am. Chem. Soc.* **44**, 1341 (1922).
[37] Lander, *J. Chem. Soc.* **83**, 412 (1903).
[38] Chapman, *J. Chem. Soc.* **127**, 1992 (1925).

$C_6H_5CON(C_6H_5)_2$. The conditions[39] had previously been stated to be 240° and 1 hour but Chapman showed this to be in error. Chapman also reported the following rearrangements:

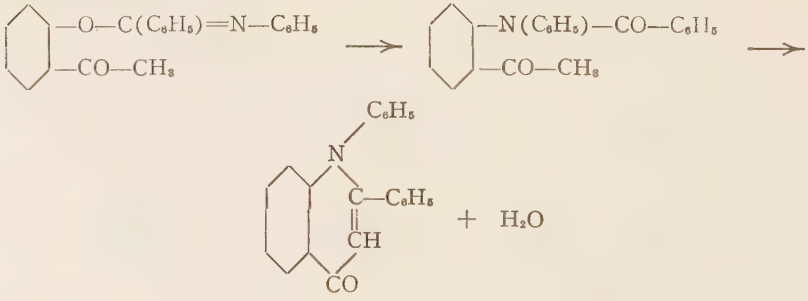


(There is no orientation of the substituents during the wandering of the aryl groups.)



When mixtures of the latter substance, *N*-tolylbenzimido tolyl ester, and *N*-phenylbenzimido phenyl ester are heated at 290°, it was shown by the method of mixed melting points that only the same two benzamide derivatives are formed that would have been anticipated had either pure compound have been heated alone. No $C_6H_5—CO—N(C_6H_5)—C_6H_4CH_3$ was ever found.

By heating *O*-acetylphenyl *N*-phenylbenzimino ether[40] there is produced not only the anticipated disubstituted benzamide, but also the dehydration product of it, namely, 1,2-diphenyl-4-quinolone. The steps are as follows:



The formation of the quinolone ring is, of course, dependent on the presence of the *o*-acetyl group. The normal rearrangement into the substituted benzamide occurs with *N*-2,4,6-trichlorophenyl-benzimino 2,4,6-trichlorophenyl ether at 280-300°:

$$C_6H_2Cl_3—O—C(C_6H_5)=N—C_6H_2Cl_3 \longrightarrow C_6H_5CO—N(C_6H_2Cl_3)_2.$$

[39] Munn, Hesse and Volquartz, *Ber.* **48**, 379 (1915).
[40] Chapman, *J. Chem. Soc.* **1927**, 1743.

It is obvious that such studies as these should lead to a means of determining the affinity capacity of the radicals which wander, and Chapman has determined the percentage change of the *N*-phenylbenzimino ethers, R—O—CPh=NPh, in 90 minutes. The radicals, *R*, may be arranged, as a result of this study, in the following descending ease of migration: *o*-nitrophenyl > 2,4,6-trichlorophenyl > *p*-acetylphenyl > 2,4-dichlorophenyl > *o*-chlorophenyl > *m*-chlorophenyl > *p*-chlorophenyl and *α*- and *β*-naphthyl > phenyl > *o*-anisyl > *m*-anisyl > *p*-anisyl > methyl.

This series is in the same order as that of the dissociation constants of the corresponding acids and phenols. Therefore, the relative attraction for electrons, and the velocity of migration of these radicals is of the same order. Furthermore, since *ortho*-substituted compounds rearrange more rapidly than the *meta* or *para* isomers, steric effects must be negligible. It is interesting to note that this method lists the methyl group at the end of the series; in other words, it is less electronegative than any of the aryl radicals, and this is what other methods for the determination of relative electron attractions also show (see pp. 26-39). However, this method is at variance with others in placing the anisyl radicals between phenyl and methyl.

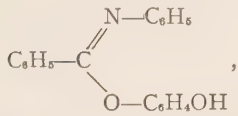
Although in this type of compound, the group attached to the oxygen is the only one that "wanders", nevertheless the groups attached to the nitrogen, Ar—O—CAr=NR, and the groups attached to the carbon, Ar—O—CR=NAr, also influence the ease of migration of the wandering group. In the first type, the ease of migration of the phenyl group attached to oxygen is influenced by the group *R*, in accordance with the following series: *p*-anisyl > phenyl > *p*-chlorophenyl and *α*-naphthyl > *m*- and *o*-chlorophenyl and 2,4-dichlorophenyl > 2,4,6-trichlorophenyl. Practically the same series is found in the second type: *p*-anisyl > phenyl > *p*- and *o*-chlorophenyl > *p*-nitrophenyl > 2,4,6-trichlorophenyl. Both of these series are in the reverse order of their electron attractions as determined by the above method, and it seems clear, therefore, that the greater the attraction of the group *R* for electrons in either type (in other words, the greater its electron attraction), the less readily will the oxygen atom release the electrons which bind it to the phenyl group, and consequently the lower will be the velocity of rearrangement of the imino ether.

N-Phenylbenzimino phenyl thioether is mostly unchanged [41] after 2 hours' heating at 280-290°, but a small amount of the thioamide, $C_6H_5CS—N(C_6H_5)_2$, is formed. At 320° or above, the breakdown is

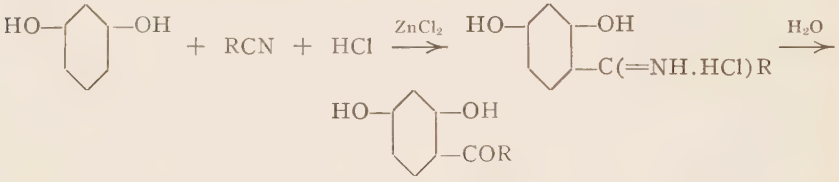
[41] Chapman, *J. Chem. Soc.* **1926**, 2296.

more complete into diphenyl sulfide, benzonitrile, thiophenol and 1-phenyl-benzothiazole. The homolog, *N*-*p*-tolylbenzimino *p*-tolyl thioether produces 1-phenyl-5-methyl-benzothiazole at 280-290°, indicating either its formation by the elimination of the group from sulfur, or previous migration of this group to nitrogen.

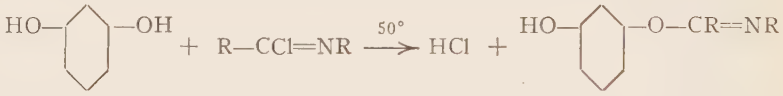
The fact [42] that *m*-hydroxyphenyl *N*-phenylimidobenzoate,



, is stable at 160° is of interest in connection with the mechanism of the Hoesch reaction [43] as proposed by Stephen. In the Hoesch reaction, nitriles unite with certain phenols in the presence of hydrogen chloride and anhydrous zinc chloride to give ketones according to the following equations:

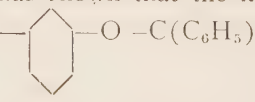


Stephen used resorcinol with substituted imino chlorides, R—CCl=NR, and explained the reaction in two steps:

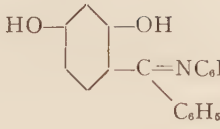
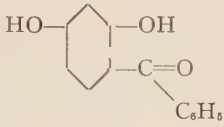
(1) 

and after the hydrogen chloride evolution had ceased:

(2)

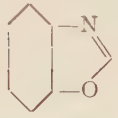
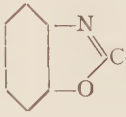
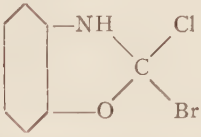
The latter reaction is one which deals with compounds like Chapman's, but the results are quite different. It may be assumed that some of the hydrogen chloride was not expelled in the first step (Stephen). In such a case, the second step would involve the pyrolysis not of the free ether but of its hydrochloride. Such compounds have been shown to behave quite differently. Chapman has shown that the hydrochloride of the compound in question, 

[42] Chapman, *J. Chem. Soc.* **121**, 1676 (1922); **123**, 1150 (1923).
[43] Hoesch, *Ber.* **48**, 1122 (1915); Stephen, *J. Chem. Soc.* **117**, 1529 (1920); Langley with Adams, *J. Am. Chem. Soc.* **44**, 2323 (1922).

changes at 160-175° and 25 mm. into  , which after hydrolysis gives  in 20 percent yield.

HYDROCHLORIDES OF *N*-ARYLBENZIMIDO ARYL ESTERS.

Concerning the structure of this class of compounds, originally it was thought that the nitrogen atom in the salts of the imino ethers was of the ammonium type; that is, $R—O—CR{=}NH_2Cl$. An alternative structure, $R—O—\underset{\displaystyle Cl}{\underset{|}{CR}}—NH_2$, was proposed by Stieglitz,[44] who offered the following evidence in its behalf.

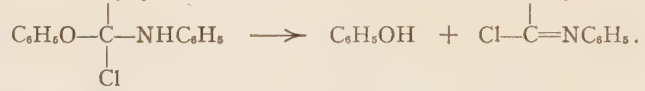
(1)  + HBr, and  + HCl, both give 

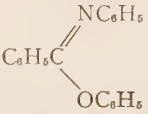
(2) Symmetrical diphenyl urea does not add hydrogen chloride, whereas carbodiphenylimide, $C_6H_5N{=}C{=}NC_6H_5$, adds 2HCl with great readiness, yielding $C_6H_5NH—CCl_2—NHC_6H_5$. The latter compound evolves hydrogen chloride at 130°, a decomposition[45] which becomes violent at 145°. Presumably, a carbodiphenylimide is formed.

The basis for the structure of carbamyl chloride could also have been used as an argument. It is generally admitted that the structure is $NH_2—CO—Cl$ and not $Cl—NH_2{=}CO$. The fact that the imino esters pyrolyze differently from their hydrochlorides may be taken as another bit of evidence that the structures of the two types are different. It is recognized that these data are not to be taken as absolute proof of Stieglitz' structure, but the evidence at least is fairly satisfactory and it shall be used in the cases which follow.

A study of the behavior of the pyrolysis[42] of the hydrochloride of phenyl *N*-phenylimidobenzoate indicates that the chief reaction is:

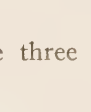
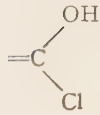
[44] Stieglitz, *Am. Chem. J.* **21**, 101 (1899).
[45] Lengfeld and Stieglitz, *Am. Chem. J.* **17**, 108 (1895).



Two experiments may be cited: one, in which the hydrochloride is heated at 150-170° in an atmosphere of carbon dioxide, and a second, similar, except for an atmosphere of dry hydrogen chloride. In the first, there results a 50 percent crude yield (18-37 percent pure yield) of the free ether,  . Assuming the correctness of the general equation above, this must have formed as a reaction product of phenol and the phenylimino-benzoyl chloride with hydrogen chloride evolution: $C_6H_5O—[H + Cl]—C(C_6H_5)=NC_6H_5$. Some phenyl benzoate and phenol are also formed. Traces of water give rise to the presence of a small amount of benzanilide (from phenylimino-benzoyl chloride). As high as 18 percent yield of an amidine hydrochloride, $C_6H_5—CCl(NHC_6H_5)_2$, also is formed, but its presence has not as yet a satisfactory explanation.

The obvious purpose of the hydrogen chloride in the second experiment is to preserve the two initial products of the reaction and to prevent the formation of any of the free ether. With such conditions, about 52-62 percent of phenylimino-benzoyl chloride and 35-33 percent of phenol are formed, and separated by fractional distillation.

The toluene derivative, $C_6H_5—O—CCl(C_6H_5)—NH—C_6H_4CH_3(p)$, behaves similarly:

It should be noticed that an unsubstituted compound of this type would possess the structure, , and it need not be stressed in detail that any one of the three combinations,  or or  , is an unstable one (see p. 21) and under various conditions

passes readily into the carbonyl group, $=C=O$ or its ammono analog, $=C=NH$. Thus, it is not surprising to learn that alkyl compounds of this type, $\begin{matrix} R'OCR{-}NHR \\ | \\ Cl \end{matrix}$, pyrolyze with the elimination of alkyl chloride instead of the elimination of alcohol. Usually, then, the products are $R'Cl + R{-}CO{-}NHR$.

The hydrochloride of ethyl imidobenzoate [46] pyrolyzes smoothly into benzamide and ethyl chloride:

$$C_6H_5{-}\underset{\displaystyle NH_2}{\overset{\displaystyle Cl}{\overset{|}{C}}}{-}OC_2H_5 \longrightarrow C_6H_5{-}CO{-}NH_2 + C_2H_5Cl.$$

Similarly,[47] the hydrochloride of ethyl imidoacetate changes by heating into ethyl chloride and acetamide; and the hydrochloride of ethyl imidomandelate,[48] $C_6H_5{-}CHOH{-}CCl(NH_2){-}OC_2H_5$, into ethyl chloride and mandelamide.

It might be anticipated that the hydrochloride of ethyl iminoformate should behave similarly. However, due to the instability of formamide, which breaks into carbon monoxide and ammonia, the observed products are ethyl chloride, formamidine hydrochloride, ethyl formate and some ammonium chloride. A recent interesting observation [49] is that trichloroacetonitrile reacts with methyl (or ethyl) alcohol in the presence of hydrogen chloride, but that the products formed are methyl (or ethyl) chloride and trichloroacetamide. The intermediate salt, $Cl_3C{-}CCl(NH_2){-}OR$, could not be isolated.

This type of decomposition is characteristic also in aliphatic compounds in which the imino hydrogen is substituted by alkyl or even by aryl groups. The intermediate compound is customarily formed by mixing an imido ester with an alkyl iodide; pyrolysis occurs by heating in a sealed tube. Thus:

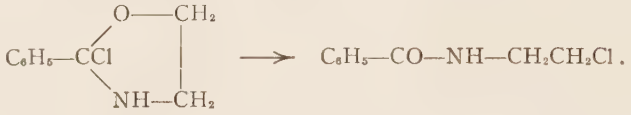
$$C_6H_5{-}CH_2{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle NH}{\overset{\|}{C}}} + CH_3I \longrightarrow \left[C_6H_5{-}CH_2{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle NH{-}CH_3}{\overset{|}{C}}}{-}I \right],$$

which decomposes [50] in one to six hours at 100° to give chiefly methyl phenylacetamide (10 grams from 30 grams of ester), $C_6H_5{-}CH_2{-}CO{-}NHCH_3$. The result does not vary widely if the methyl iodide is

[46] Pinner, *Ber.* **16**, 255 (1883).
[47] Pinner, *ibid.*, 1654.
[48] Beyer, *J. prakt. Chem.* **28**, 190 (1883).
[49] Steinkopf and Müller, *Ber.* **56**, 1930 (1923).
[50] Wheeler and Johnson, *Am. Chem. J.* **33**, 142 (1900).

present in small amounts [51] or in amounts of 0.5 mol. In all cases, during the rearrangement of several *N*-arylacetimino ethers, *N*-alkylbenzimino ethers and *N*-arylbenzimino ethers in the presence of 0.5 mol of methyl or ethyl iodide, there is apparent migration of alkyl from oxygen to nitrogen. One reaction deserves mention. Ethyl phenylimino-acetate, $CH_3—C(=NC_6H_5)—OC_2H_5$, with one mol of methyl iodide, gives *N*-methyl acetanilide completely in 8 hours at 150°.

A cyclic compound of similar type,[52] namely, phenyl oxazoline hydrochloride, pyrolyzes above its melting point, 81°, into a 90 percent yield of *N*-β-chloroethyl-benzamide:



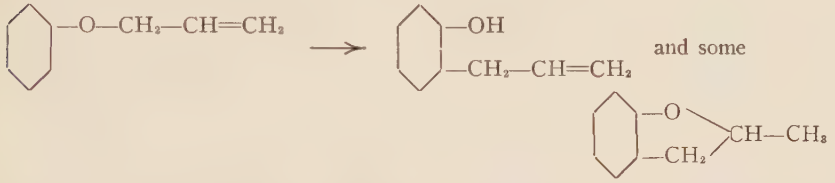
Allyl Phenyl Ethers.

It has already been mentioned on p. 206 that the allyl phenyl ethers constituted a special case which has been studied very extensively by various workers, but in particular by Claisen. It should be noted that these ethers possess not only the β,γ-unsaturation of the allyl group, but also the α,β-unsaturation of the phenyl group. The phenyl group is highly electronegative in comparison to the allyl, and therefore, the allyl is the group which becomes detached from the oxygen and wanders to the *ortho* carbon atom. The allyl group is not only very loosely bound to oxygen, but also to nitrogen, or sulfur, or halogen. Thus, recent studies in the author's laboratory indicate that allyl phenyl thioether rearranges by heating into *o*-allyl thiophenol, and that *N*-allyl anilines behave analogously. If either one of the *ortho* atoms of the aromatic nucleus is unsubstituted, the allyl group almost invariably migrates into the *ortho* position; if both, however, are substituted, *para* rearrangement occurs. In special cases it will be shown that an *ortho* substituent may be expelled by an incoming allyl group.

Preparation. *To prepare the allyl ethers,* in general the phenol is mixed with allyl bromide and potassium carbonate in acetone, and the whole refluxed for several hours. Thus, with 188 grams of phenol, 242 grams of allyl bromide, 280 grams of potassium carbonate and 300 grams of acetone an 86 percent yield of allyl phenyl ether may be secured by vacuum distillation after 8 hours of refluxing. *The technic of the rearrangement* is very simple. Usually the ether is heated at or

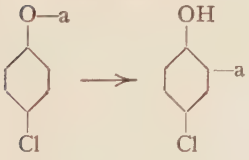
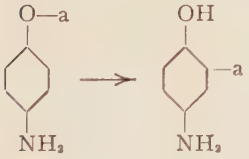
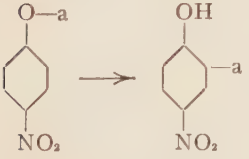
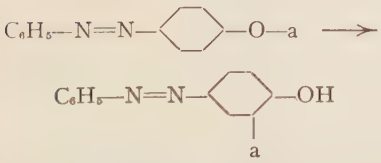
[51] Lander, *J. Chem. Soc.* **83**, 406 (1903).
[52] Wislicenus and Koerber, *Ber.* **35**, 164 (1902).

below the boiling point, sometimes in the presence of inert solvents. Frequently, the reáction is decidedly exothermic and in other cases the heat of reaction is hardly apparent. An 80 percent yield of *o*-allyl phenol comes by heating [53] the ether for 6 hours at 190-220° (i.e., at the boiling point). It may be separated from a 4-6 percent yield of methyl cumarane by dissolving the phenol in alkali, and extracting the cumarane with petroleum ether.



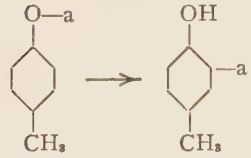
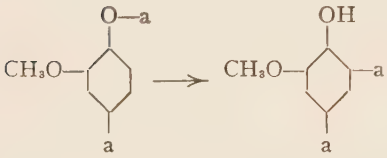
Other illustrations will be mentioned briefly; the excellence of the yields and the simplicity of the procedure should be noted. For brevity, the symbol (a) shall be used to represent allyl, $—CH_2—CH=CH_2$.

TABLE XXIII. *Preparation of Allyl Ethers (Para Position Filled).*

Reaction	Percent Yield	Conditions of Reaction
	Quantitative	Refluxing 20 minutes.
	70	6 hours at 185°, in petroleum.
	30-40	260° for a short time, or 230°, in petroleum, for a longer period.
	70	230° in petroleum for 30 to 60 minutes.

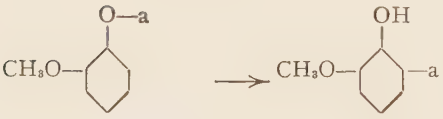
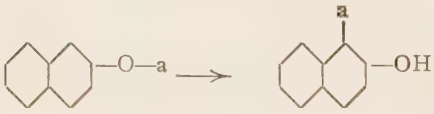
[53] Claisen and Eisleb, *Ann.* **401**, 21 (1913); Claisen, Eisleb and Kremers, *Ann.* **418**, 69, 79 (1919); Jacobs and Heidelberger, *J. Am. Chem. Soc.* **39**, 2202 (1917); Adams and Rindfusz, *ibid.*, **41**, 654 (1919); Claisen and Tietze, *Ann.* **449**, 84 (1926).

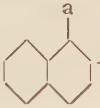
TABLE XXIII. (*Continued*)

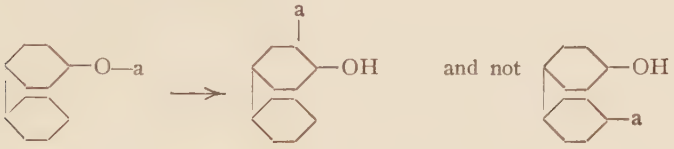
Reaction	Percent Yield	Conditions of Reaction
	80	Reflux for one hour.
	70	200° for 75 minutes.

In the illustrations which have just been given, the *para* position has been filled, but in the following table wherein both the *ortho* and *para* positions are available in the molecule, the rearrangement is still exclusively *ortho*.

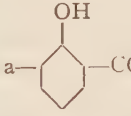
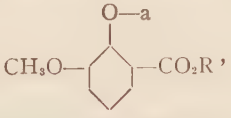
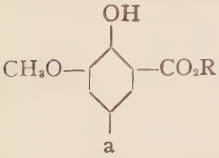
TABLE XXIV. *Preparation of Allyl Ethers (Para Position Vacant).*

Reaction	Percent Yield	Conditions of Reaction
	Quantitative	By slow distillation.
	70-80	Long refluxing.
	70	At 170-180° for a long time.
	50-60	230° for 1 hour.
	Almost quantitative	210°.

The proof of constitution for the two allyl naphthols rests chiefly on the fact that coupling with diazonium salts is possible with the α-naphthol derivative, but not with the β-. Furthermore, the allyl ether of this β-derivative,  , is stable when heated.[54] This reaction is of interest to indicate the "*ortho*" position in the naphthalene series. Another very interesting case, is the pyrolysis of the allyl ether of *p*-hydroxy-diphenyl,[55] which gives the usual *ortho* rearrangement instead of giving the *p'*-isomer. Thus:

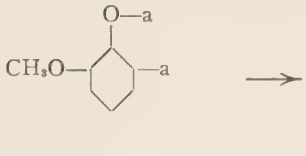
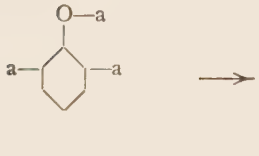
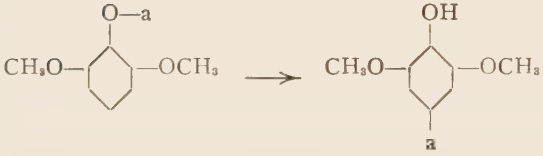


To provide a really satisfactory test, however, that the allyl group cannot migrate to the *p'*-position, both ortho groups should be blocked.

Rearrangement with Salicylates. The rearrangements with allyl ethers of salicylates are interesting. By heating the allyl ether of ethyl salicylate,[56] good yields of ethyl 3-allyl salicylate,  , are formed. The free acid may be prepared from this, if desired, by hydrolysis. If the available *ortho* position is blocked, as in  , then the rearrangement proceeds in good yields to the *para* isomer,  . By removal of the $-CO_2R$ group, there is provided a method of synthesis for eugenol. Similar cases of *para* rearrangement, when both *orthos* are blocked, are given in the following table:

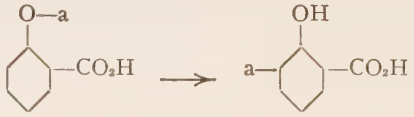
[54] *See also* Claisen, *Ber.* **45**, 3159 (1912).
[55] Gilman and Kirby, *J. Am. Chem. Soc.* **48**, 2191 (1926).
[56] Claisen and others, *loc. cit.*; Claisen, U. S. Pat. 1,094,123, Apr. 21, 1914; *Chem. Abstracts* **8**, 2032 (1914).

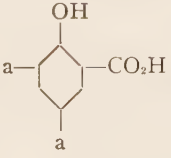
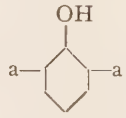
TABLE XXV. *Para Rearrangement with Both Ortho Positions Blocked.*

Reaction	Percent Yield	Conditions of Reaction
	70-80	Short refluxing.
	about 50	250-290° in a carbon dioxide atmosphere.
		At 220°.[57]

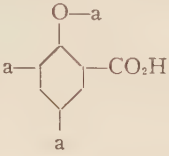
As would be expected, *meta* substituents have little effect on the reaction; the allyl ether of 3,5-dimethyl-phenol rearranges [58] smoothly by boiling until there is no longer an increase in the boiling temperature. The product of the reaction is 2-allyl-3,5-dimethyl phenol.

Claisen and Eisleb have found that the allyl ether of salicylic acid (prepared by hydrolysis of the allyl ether of ethyl salicylate) may be rearranged into an allyl salicylic acid without any accompanying evolution of carbon dioxide unless the temperature is allowed to rise too high:

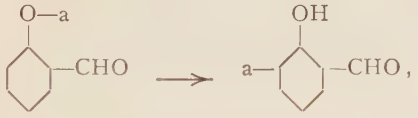


About one-third of the allyl ether of the latter compound, however, is rearranged into a diallyl salicylic acid,  ; and about two-thirds into *o,o*-diallyl-phenol,  , accompanied by evolution of carbon dioxide.

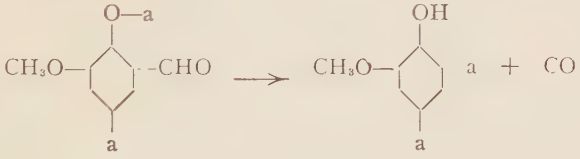
[57] Mauthner, *Ann.* **414**, 250 (1918).
[58] von Auwers and Borsche, *Ber.* **48**, 1716 (1915).

Pyrolysis of *o*-Substituted Allyl Ethers, which Involve the Elimination of the *ortho* Substituent. The above reaction, in which a carboxyl group is replaced by allyl is not an isolated case. Elimination of CO_2 begins at 100°, and ceases at 180°. The allyl ether of diallylsalicylic acid,  , pyrolyzes exclusively into triallyl-phenol, and in this case also, carbon dioxide starts to be evolved at 100°, and continues with increasing temperature.

Elimination of carbon monoxide is also a fairly common reaction, although it does not occur with the allyl ether of salicylaldehyde; instead, the normal reaction:

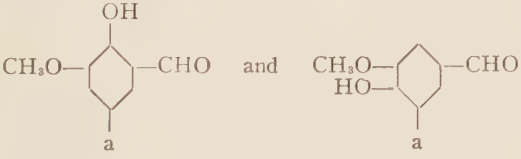


occurs easily at 220°. However, in cases such as the following, carbon monoxide is readily detached. At 170-285°:

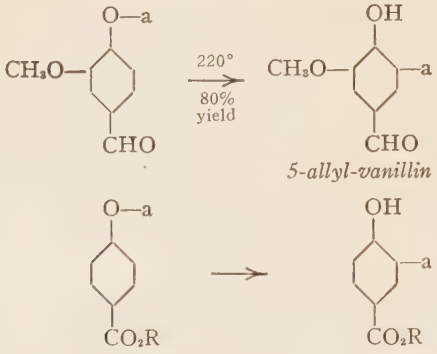


At 170-240° the reaction is chiefly:

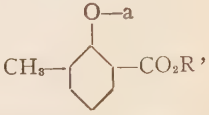
but there is also some formation of



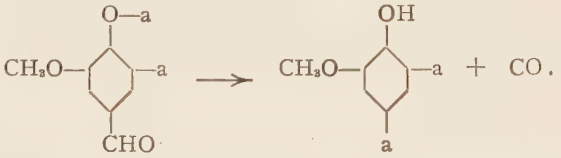
Other similar cases which should and do proceed normally are the following:



5-allyl-vanillin

The case of the allyl ether of ethyl 3-methylsalicylate, 

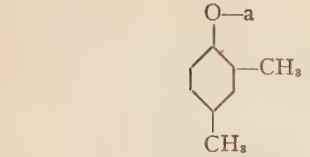
is strictly analogous to the other salicylates which have been discussed. The allyl ether of 5-allyl-vanillin loses 82 percent of the theoretical amount of carbon monoxide, giving *o*-allyl eugenol:



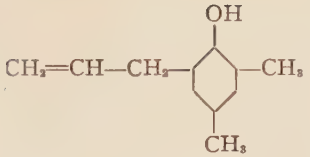
In this reaction, therefore, allyl has caused the detachment of a *para* aldehyde group.

The various possibilities of reaction for the allyl side-chain include the following. It may be oxidized to carboxyl, or catalytically reduced to *n*-propyl. If the allyl phenols are heated with alcoholic potassium hydroxide, the allyl group is isomerized to the propenyl group, —CH=CH—CH_3. Frequently, heating the allyl phenol with pyridine hydrochloride induces the cumarane formation, also an isomeric change. To illustrate some of these transformations,[59] the case of 2,4-dimethyl-phenyl allyl ether may be cited. It is changed into 2,3-dimethyl-6-allyl-phenol in 90 percent yields either by heating for 2.5 hours at 356 mm. or 2.5-3 hours at 200-210°. If this is heated with three parts of a 26 percent solution of potassium hydroxide in methanol, it gives a 95 percent yield of 2,4-dimethyl-6-propenyl-phenol. If, instead, it is heated with about 5 percent by weight of pyridine-hydrochloride it gives a 75 percent yield of 2,5,7-trimethyl cumarane.

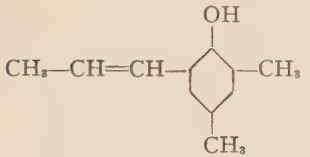
[59] Claisen and Tietze, *Ann.* **449**, 81 (1926).



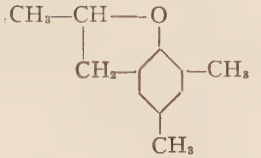
Dimethylphenyl Allyl Ether



Dimethyl Allyl Phenol



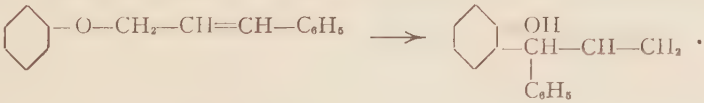
Dimethyl Propenyl Phenol

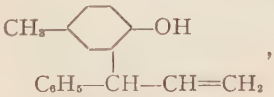


Trimethyl Cumarane

Mechanism of the Pyrolysis. Superficially, it may be thought that the rearrangement of a phenyl allyl ether into an allyl phenol merely involves a scission of the carbon-to-oxygen linkage at the allyl junction and a wandering of this radical as such to the *ortho* carbon atom. This mechanism would lead one to infer that the allyl carbon atom originally attached to the oxygen is the one which becomes attached to the nuclear carbon. However, very convincing evidence shows that this is not the case, and instead it is the *gamma*-carbon of the allyl group in the ether which becomes attached to the nucleus in the allyl phenol. If this carbon is denoted by an asterisk, the equation becomes:

With a modifying group in the allyl chain such as phenyl or bromo or methyl, it becomes possible to demonstrate the correctness of this statement. When phenyl cinnamyl ether[60] is heated, the product of the reaction is not *o*-cinnamyl phenol but instead is *o*-*α*-phenylallyl phenol:



Similarly, the homolog, 

, is prepared in 70 percent yield by heating the cinnamyl ether of *p*-cresol. Other cases will be mentioned briefly, but they are all indicative of this general plan of rearrangement, as is shown in the following reactions:[61, 62]

[60] Claisen and Tietze, *Ber.* **58**, 275 (1925).
[61] *Ibid.*, *Ber.* **59**, 2344 (1926).
[62] von Braun, Kühn and Weismantel, *Ann.* **449**, 249 (1926).

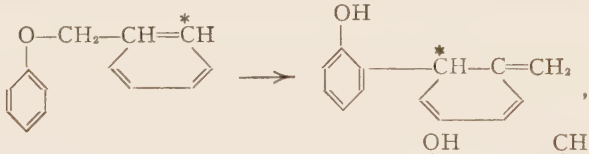
$$C_6H_5—O—CH_2—CH=CH—CH_3 \longrightarrow o\,C_6H_4\langle^{OH}_{CH(CH_3)—CH=CH_2}$$

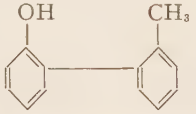
$$C_6H_5—O—CH_2—CH=C(CH_3)_2 \longrightarrow o\,C_6H_4\langle^{OH}_{C(CH_3)_2—CH=CH_2}$$

$$C_6H_5—O—CH_2—CBr=CH_2 \longrightarrow o\,C_6H_4\langle^{OH}_{CH_2—CBr=CH_2}$$

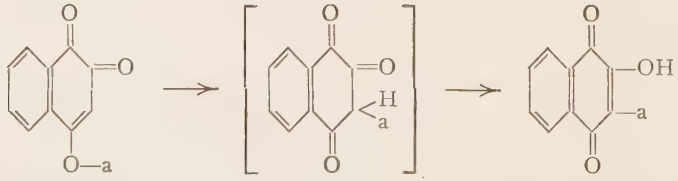
A 30 percent yield is obtained by heating 10 parts of β-bromoallyl phenyl ether with 2 parts of decalin at the boiling point of the mixture (about 215°).

With this mechanism, it is not difficult to understand why it is that phenyl benzyl ether (p. 202) does not pyrolyze into *o*-benzyl phenol. Both the benzyl and the allyl groups possess β,γ-unsaturation, and both are well towards the positive end of the electronegativity series. However, for phenyl benzyl ether to rearrange, the following steps would be anticipated:



which in turn would then rearrange into  . It can readily be imagined that the tendency for such a transformation would be slight.

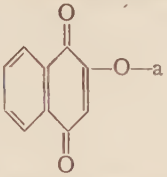
It is quite possible that there is an intermediate quinone stage in the rearrangement of phenyl allyl ethers into allyl phenols. In fact, Fieser [63] has postulated such a mechanism in the rearrangement of allyloxy naphthoquinones at about 130-135° (about 5° above the melting point).

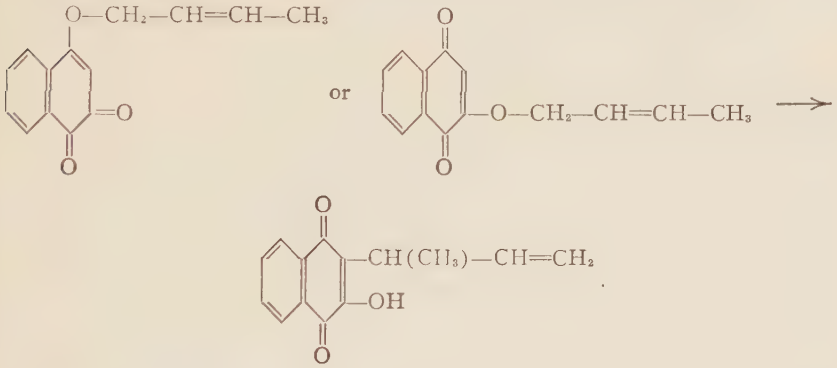


4-Allyloxy-1,2-naphthoquinone *2-Allyl-3-hydroxy-1,4-naphthoquinone*

The phenol is formed in 14 grams yield (pure) from 20 grams of the ether; the reaction is highly exothermic. The same phenol compound

[63] Fieser, *J. Am. Chem. Soc.* **48**, 3205 (1926); **49**, 857 (1927).

is formed, and the same quinone intermediate product is formed if the isomer,  , is selected as the starting material. In this case, the reaction is much less exothermic. If the crotyl ethers are used in place of the allyl ethers, the reactions are quantitatively completed in 20-30 minutes at a little above the respective melting points (120° for the *o*-quinone ether and 137° for the *p*-form). Thus, either

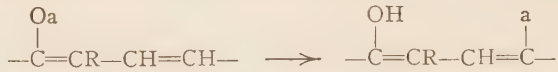


If the intermediate quinone structure (see also p. 206) proves to be correct, then the similarity of the rearrangement of the allyl phenyl ethers to other enol ethers or to imino ethers will be complete. Certainly, α,β-unsaturation, such as is present in the phenyl group (or in enol ethers or in imino ethers) is essential, for Claisen[64] has shown that there is no rearrangement of allyl cyclohexyl ether even after several hours in a sealed tube at 210°. Purely aliphatic compounds,[65] such as *O*-allyl acetoacetic ester, which possess α,β-unsaturation rearrange also in this manner.

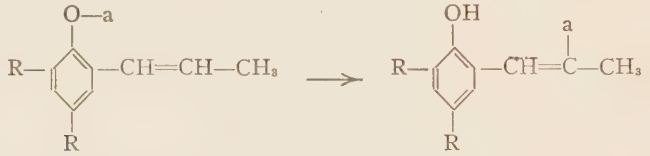
The rearrangement of an allyl group to an *ortho* carbon atom involves the following change:

[64] Claisen, Eisleb and Kremers, *Ann.* 418, 97 (1919).
[65] Claisen, *Ber.* 45, 3157 (1912).

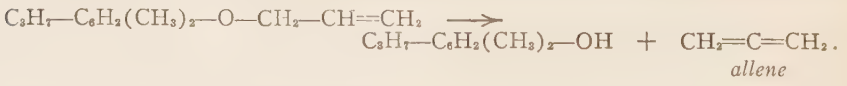
and the rearrangement to a *para* carbon atom, the following change:



If both *ortho* positions and the *para* position are blocked, it is still possible to have rearrangement if the condition of unsaturation is fulfilled in the side chain. The vinyl or propenyl groups satisfy this condition. Thus, the transformation of



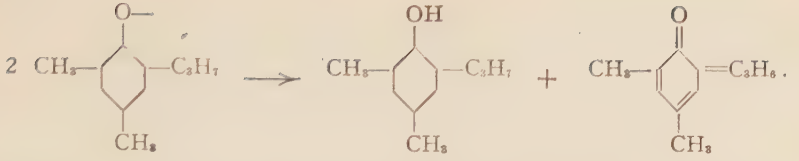
proceeds satisfactorily in the cases[66] wherein it has been studied. In these cases, the *R* groups have been methyl and methyl; chlorine and chlorine; and *o*-methoxy and *p*-propyl. The best conditions for rearrangements of this type appear to be refluxing for about 5 hours under a reduced pressure so that the boiling temperature is about 160-175°, usually at 15-50 mm. pressure. A hydrogen atmosphere may be employed. The yields are good but not as satisfactory as in the cases wherein the allyl group migrates to the aromatic nucleus. Side reactions lead to either resinification, or to a definite scission of the allyl group so that it appears as *allene* or *diallyl*. One case deserves especial mention. If the allyl ether of 2,4-dimethyl-6-propyl-phenol is heated for 15 minutes at 210-250°, a 10 percent yield of pure allene gas, and a 50 percent yield of diallyl are formed. A fairly good yield of the phenol (propyl xylenol) is obtainable, and lesser amounts of resinous matter. Claisen suggests two reactions to account for these changes. In the first, allene is formed directly, but this is the lesser of the two reactions:



In the second, the allyl radical is considered to be formed momentarily. It polymerizes to diallyl:

The other aryloxy radical is thought to undergo a disproportionation into the propyl xylenol and resinified propylidene xyloquinone:

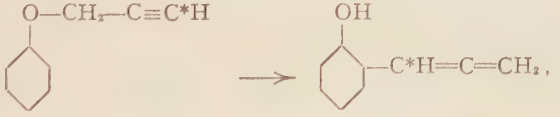
[66] Claisen and Tietze, *Ann.* 449, 84, 94 (1926).



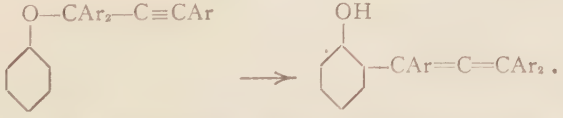
Phenyl Propargyl Ether, and Related Compounds.

The propargyl group is similar to the allyl group in containing β,γ-unsaturation, but when phenyl propargyl ether, $C_6H_5—O—CH_2—C\equiv CH$, is boiled, or is heated [67] in di-*iso*amyl ether (an inert solvent), the only product of the reaction is a black tar, not at all soluble in alkali. *p*-Bromophenyl propargyl ether behaves similarly. Phenoxyacetonitrile, $C_6H_5—O—CH_2—C\equiv N$, with similar β,γ-unsaturation, may be recovered in 90 percent amounts after 15 hours of refluxing. Its homolog, *p*-methyl-phenoxyacetonitrile, becomes completely resinified after 24 hours of boiling, whereas it is largely unchanged in boiling *iso*amyl ether. A small amount of *p*-cresol forms in the latter case.

If the mechanism of the pyrolysis of the propargyl ethers follows that of the allyl ethers, the anticipated products would be allenes, and not propargyl phenols. It is easy to see, therefore, why it is that tars and polymeric products are formed in these reactions, because of the reactivity of the allene nucleus. The initial step in the pyrolysis may be as follows:

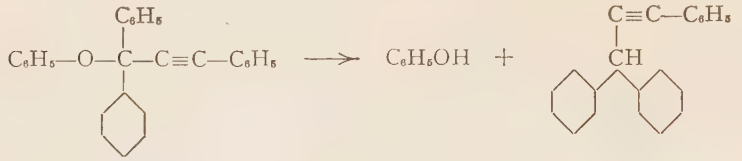


which polymerizes. If this is correct, it is reasonable to assume that tetrasubstituted allenes, which are comparatively stable, might be prepared by heating phenyl triarylpropargyl ethers:

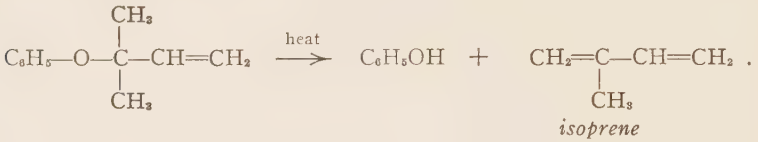


This method is being studied in the author's laboratory at the present time. Preliminary results, however, seem to indicate that phenol and 9-phenylethynyl-fluorene are formed instead, by heating in a test-tube to about 300°. This indicates the following reaction:

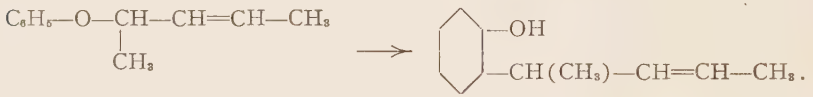
[67] Powell and Adams, *J. Am. Chem. Soc.* **42**, 654 (1920).



Other compounds of a related type wherein the aryl groups are largely replaced by alkyls may permit the desired reaction; this is being studied at the present time. There is chance that here also the reaction may go astray, and indeed Claisen [67a] has noted the following reaction:



This and similar reactions have also been observed in the author's laboratory. A tertiary group, in the cases studied, appears to inhibit the rearrangement. There is some evidence that secondary groups with the allyl configuration also give phenol on heating, but Claisen [67b] has reported a 70-80 percent yield of normal rearrangement product after 20 minutes' heating (205-225°) of phenol-α,γ-dimethylallyl ether:



Search is still in progress for a compound of this structure, but with a tertiary allyl group linked to the oxygen, which may rearrange normally on heating. If successful, this method should offer interesting possibilities for the synthesis of allenes with substituents on the aromatic nucleus such as carboxyl, or dimethylamino, which are almost impossible to prepare by the present methods of synthesis. In this way, an avenue of approach is laid for the synthesis [68] of optically active allenes.

Allyl Ethers of Catechol and Resorcinol.

None of Claisen's work has dealt with the rearrangement of dihydric phenols, but it has recently been found [69] in the author's laboratory that the allyl ethers of catechol and substituted catechols may be prepared in good yields by the general methods which are satisfactory

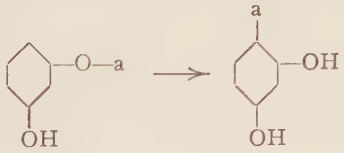
[67a] Claisen, Kremers, Roth and Tietze, *J. prakt. Chem.* **105**, 67 (1922).
[67b] Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 226 (1925).
[68] Hurd and Cohen, unpublished results. *See also* Hurd and Webb, *J. Am. Chem. Soc.* **49**, 546 (1927).
[69] Hurd and Greengard, unpublished results, presented in part at the Richmond meeting of the American Chemical Society, April, 1927.

for the allyl ethers of phenols; and furthermore, that these ethers of catechol compounds pyrolyze in the normal manner preferentially to the *ortho* position, to a lesser extent to the *para* position, and none to the *meta* by simple heating. The same is true for compounds of resorcinol. Briefly, the results are as follows.

The monoallyl ether of catechol gives 3-allyl catechol between 175-210° with a slight exothermal reaction. Some of the 4-allyl isomer is also formed in this process.[70] The diallyl ether of catechol gives a very vigorous exothermal reaction at about 180°, the temperature of the liquid rising quickly to about 280°. In this manner there is an almost complete conversion into 3,6-diallyl catechol (both allyl groups becoming detached from the oxygen). If 3-allyl catechol, prepared as above, is converted into its monoallyl ether, the substance formed is undoubtedly 1-allyloxy-6-allyl-phenol, for on pyrolysis it yields 3,6-diallyl catechol also. The diallyl ether of 3-allyl catechol undergoes pyrolysis into triallyl catechol, and the diallyl ether of 3,6-diallyl catechol rearranges at about 200° into tetraallyl catechol.

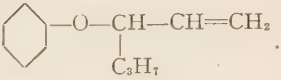
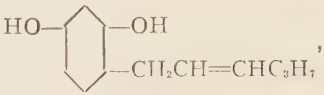
The geranyl group is related to the allyl group, and Kawai [71] has found that catechol geranyl ether (crude) on vacuum distillation appears to undergo rearrangement.

The monoallyl ether of resorcinol gives about an 86 percent yield of 1-allyl-2,4-dihydroxybenzene at a temperature of 190-220°. This reaction is somewhat exothermic. The structure of the new compound was established by methylation and oxidation to 2,4-dimethoxybenzoic acid. Thus:

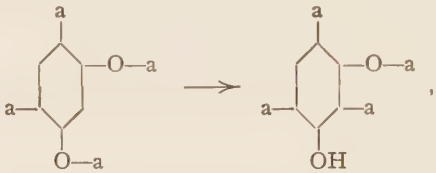


The *ortho* position between the two hydroxyls seems to be avoided. This suggests an interesting method of synthesis for *n*-hexyl resorcinol which is being studied in the author's laboratory. Thus, from acrolein and *n*-propyl magnesium bromide it has been possible to synthesize propyl vinyl carbinol (unless rearrangement into hexene-2-ol-1 occurred, and some evidence points to this) which may be used

[70] Kawai, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 3, 263 (1925); Perkin, Jr., and Trikojus, *J. Chem. Soc.* 1927, 1663.
[71] Kawai, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo) 6, 53 (1927); *Chem. Abstracts* 22, 381 (1928).

as an intermediate in the synthesis of the mono-α-n-propylallyl ether of resorcinol,  . On heating, this may undergo at least two reactions. The ether may divide into resorcinol and hexadiene-1,3, or it may undergo normal rearrangement into (2,4)-dihydroxy-phenyl-1-hexene-2,  , which on reduction should yield hexyl resorcinol. Preliminary work indicates that the former reaction, the undesired reaction, is the major one.

The diallyl ether of resorcinol rearranges in the normal manner into 1,5-diallyl-2,4-dihydroxybenzene. The diallyl ether of the latter substance still has two available nuclear carbon atoms, but one of them is *meta*. Therefore, it would be anticipated that only one of the two allyl groups should be affected by the heating:



and such was actually found to be the case.

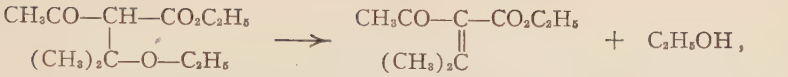
The allyl ethers of other polyhydroxy-benzenes have not been studied, but an interesting possibility regarding the possible behavior of the allyl ethers of phloroglucinol has been mentioned on p. 206.

In this connection [72] it may be of interest to note that the allyl derivatives of thiophenol and of aniline also rearrange in a similar manner by refluxing. Aniline, in the "ammonia system", is related to phenol in the "water system". Therefore, it should be expected that allyl phenyl amine should rearrange to a primary amine by heating, and it has been found that it does so. These cases will be discussed in a later chapter. (See p. 295.)

More Complex Ethers, which Frequently Give Alcohols as Decomposition Products.

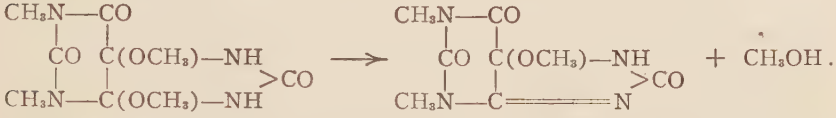
α-Ethoxy*iso*propyl-acetoacetic ester [73] is a rather unstable substance. It decomposes gradually at room temperature into alcohol and ethyl α-acetyl-β-methyl-crotonate:

[72] Hurd and Greengard, unpublished results.
[73] Merling and Welde, *Ann.* 266, 135 (1909).



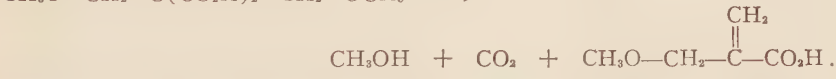
but there is also a minor decomposition into ethyl acetate and β,β-dimethyl acrylic ester.

By simple heating of the dimethyl ether of 1,3-dimethyluric acid glycol [74] either at 160° in a vacuum or by heating in glacial acetic acid solution, methanol is liberated. The reaction is nearly quantitative.



If 5,6-dihydroxy-5-ethoxy-5,6-dihydrouracil [75] is anhydrous, it changes at 160° into *iso*dialuric anhydride:

Methoxymethacrylic acid [76] may be formed by the pyrolysis of bis-methoxymethyl-malonic acid at 140°.



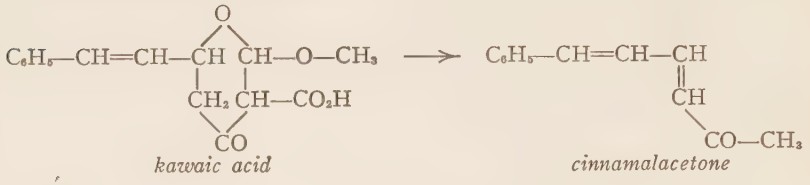
Helferich and Fries [77] have recently shown that distillation (170-220°) of γ-hydroxyvaleraldehyde-dimethyl-acetal completely converts it into a ring compound with the elimination of methanol. However, it was

found to be distillable in the presence of barium oxide. Harries [78] reported that the semi-acetal of glyoxal, $CHO—CH(OC_2H_5)_2$, boils with some decomposition at 80-90°, giving glyoxal and alcohol as the products of the change. Small yields [79] of aldehydo-propionic acid, $HO_2C—CH_2CH_2—CHO$, are produced when acetal-malonic acid, $(HO_2C)_2CH—CH_2—CH(OC_2H_5)_2$, is heated and then distilled *in vacuo*. Since the same reaction is produced when the heating is carried out in the presence of water, Perkin and Sprankling thought that the

[74] Biltz and Strufe, *Ann.* **413**, 164 (1917).
[75] Biltz and Paetzold, *Ann.* **452**, 76 (1927).
[76] Kleber, *Ann.* **246**, 97 (1888).
[77] Helferich and Fries, *Ber.* **58**, 1246 (1925).
[78] Harries, *Ber.* **36**, 1935 (1903).
[79] Perkin and Sprankling, *J. Chem. Soc.* **75**, 11 (1899).

elimination of carbon dioxide and alcohol was due "to the unavoidable presence of small quantities of water".

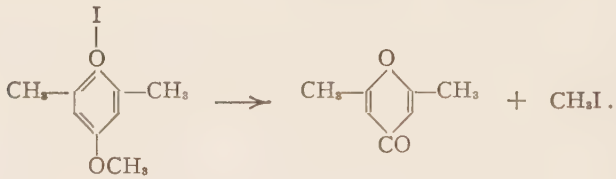
The following decomposition [80] occurs by distillation in a vacuum:



kawaic acid *cinnamalacetone*

It may be inferred that carbon dioxide and methyl formate, $CH_3O—CHO$, are detached. Methyl formate would be expected to break into two molecules of formaldehyde, but this was not mentioned. Cinnamalacetone is also produced when the decarboxylated derivative of kawaic acid is distilled [81] in a vacuum.

Dimethylpyrone-iodomethylate undergoes pyrolysis [82] at 100° into methyl iodide and dimethyl pyrone:



The difference in stability of the triethylidene [83] derivative of mannitol and the tribenzal [84] derivative, $C_6H_8\left(\begin{matrix}—O\\—O\end{matrix}>CH—C_6H_5\right)_3$, is quite marked. The former boils without decomposition at 285°, whereas the latter melts with decomposition at 213-218°. Formaldehyde dibenzylacetal undergoes a disproportionation reaction [85] at 330°:

$$(C_7H_7O)_2CH_2 \longrightarrow [(C_7H_7)_2O] + HCHO$$
$$[(C_7H_7)_2O] \longrightarrow C_6H_5CH_3 + C_6H_5CHO.$$

[80] Murayama and Shinozaki, *J. Pharm. Soc. Japan* No. 516, 185 (1925); *Chem. Abstracts* 19, 1706 (1925).
[81] *See also* Borsche and Rath, *Ber.* 54, 2229 (1921) for a different structure for kawaic acid.
[82] Kehrmann and Duttenhoefer, *Ber.* 39, 1302 (1906).
[83] Meunier, *Ann. chim.* [6] 22, 416 (1891).
[84] de Bruyn and van Ekenstein, *Rec. trav. chim.* 18, 151 (1899).
[85] Carré, *Compt. rend.* 186, 1629 (1928).

CHAPTER 9.

PEROXIDES.

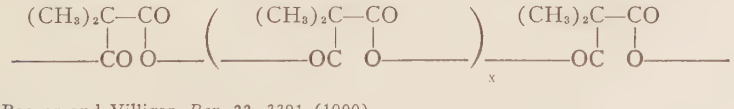
Diethyl peroxide boils at 65°; it explodes,[1] however, in contact with a warm glass rod (a thermometer registering 250°). The spontaneous decomposition of triphenylmethyl peroxide[2] is assumed to result in the formation of a radical, $(C_6H_5)_3C—O—$, most of which (60-70 percent) rearranges into phenoxydiphenylmethyl, $C_6H_5—O—C(C_6H_5)_2$. In turn, this polymerizes into the major product of the reaction, namely, diphenyl-benzopinacol, $C_6H_5O—C(C_6H_5)_2—C(C_6H_5)_2—OC_6H_5$. This change occurs by boiling the peroxide in xylene. The diphenylbenzopinacol reverts into phenoxydiphenylmethyl at 230-240° (bath, 280°), in the absence of air; and at this temperature is transformed in about 75 percent yields into tetraphenylethylene and diphenoxydiphenylmethane:

$$4[C_6H_5—O—C(C_6H_5)_2] \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2(C_6H_5)_2C(OC_6H_5)_2$$

Small quantities of phenol also result.[3] No oxygen is evolved from the peroxide up to 250°.

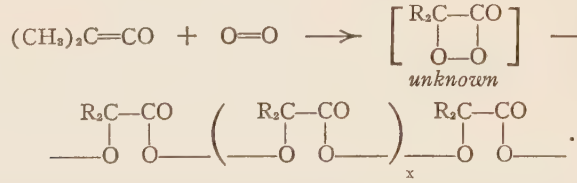
Rubrene peroxide,[4] which is formed by shaking a solution of rubrene in benzene with air until the color disappears, and then removing the solvent, is a white crystalline substance that evolves oxygen at 100°, rapidly at 150°, and completely at 200°. Eighty-seven percent of the calculated amount of oxygen is collected, and light is evolved in the process.

Staudinger[5] has proposed a mechanism for the reactions of peroxides which is stimulating. Just as malonic anhydrides are unstable except in the polymerized form,

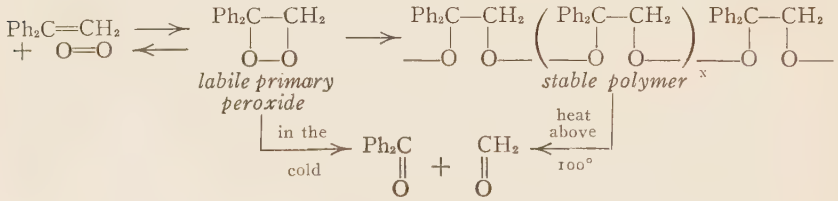


[1] Baeyer and Villiger, *Ber.* **33**, 3391 (1900).
[2] Wieland, *Ber.* **44**, 2550 (1911).
[3] Pummerer and Frankforter, *Ber.* **47**, 1480 (1914).
[4] Moureau, Dufraisse and Dean, *Compt. rend.* **182**, 1584 (1926); Moureau, Dufraisse and Girard, *ibid.* **186**, 1027 (1928).
[5] Staudinger, *Inst. Intern. Chim. Solvay, 2ième Cons. Chim.* **1926**, 594.

which is an amorphous polymer that pyrolyzes into dimethyl ketene and carbon dioxide, so also dimethyl ketene peroxide is amorphous and insoluble:



The diphenyl ketene derivative gives some benzophenone and carbon dioxide even in the cold. Similarly, diphenyl-ethylene peroxide becomes transformed into benzophenone and formaldehyde:



Diacyl Peroxides.

Dipropionyl peroxide, $(C_2H_5CO)_2O_2$, is less explosive than the diacetyl compound. It decomposes explosively at 80°, but at 60° the evolution of gases is quite gradual. The gases [6] have the following analysis: 58.4 percent carbon dioxide, 16.9 percent butane, and 24.7 percent methane. Traces of ethyl propionate are also formed. This work, and later work with succinyl peroxide, has been used [7] in the interpretation of the mechanism of hydrocarbon formation in the electrolysis of salts of fatty acids (Kolbe's synthesis). Fichter favors the mechanism originally proposed by Schall, which states that acid peroxides are first formed at the anode; hydrocarbons then come by the decomposition of these peroxides:

$$R—CO_2—CO_2—R \longrightarrow R—R + 2CO_2.$$

Walker, however, opposes this view, and cites the fact that methane is always a product of pyrolysis but is never found in the anode gases.

By heating succinyl peroxide in a bomb at 180° (some air present), the volume relationship of the gaseous reaction products are as follows: carbon dioxide, 55 percent; ethylene, 21 percent; methane, 6.9 percent; carbon monoxide, 6.5 percent; nitrogen, 9.7 percent; and oxygen, 0.6

[6] Fichter and Krumnenacher, *Helv. Chim. Acta* 1, 146 (1918).
[7] Fichter and Fritsch, *ibid.* 6, 329 (1923); Walker, *J. Chem. Soc.* 1928, 2040.

percent. The instability of succinyl peroxide above 110° has also been noted[8] by Gilman and Adams. A mixed peroxide, acetyl peroxide succinic acid, if heated[9] in a bomb at 180° for 10 minutes, gives a 94 percent yield of carbon dioxide and an 88.5 percent yield of *n*-butyric acid,

$$CH_3CO{-}O{-}O{-}CO{-}CH_2CH_2CO_2H \longrightarrow 2CO_2 + CH_3CH_2CH_2CO_2H.$$

This, again, is confirmatory evidence for the intermediate formation of peroxides in Kolbe's electrochemical synthesis of hydrocarbons, since it is similar to the electrochemical synthesis of ethyl butyrate from a mixture of potassium acetate and potassium ethyl succinate. Evidence against the formation of free radicals[10] in Kolbe's synthesis was furnished by Erlenmeyer. He found that only traces of methyl bromide or of methyl iodide are formed when a 40 percent potassium acetate solution is electrolyzed in the presence of bromine or iodine. It is merely a side reaction, since an equivalent amount was formed from $CH_3{-}CO{-}O_2H + NaBr + CH_3CO_2H$ at 60°. Another unsymmetrical peroxide, acetyl benzoyl peroxide, also furnishes[11] interesting confirmatory evidence regarding the mechanism. If this compound is exploded in a bomb at 200°, toluene is formed, and this decomposes in part into ethane, benzene and diphenyl. Strictly speaking, however, these are not the exclusive pyrolytic products of toluene as was shown on pp. 103, 105. If a mixture of diacetyl peroxide and dibenzoyl peroxide is heated in a similar manner, no toluene is formed; benzene and diphenyl are the reaction products, and more diphenyl is formed in this experiment than in the other case. These investigators also demonstrated the absence of methyl iodide when diacetyl peroxide and iodine are exploded together. These experiments show that the radicals *methyl* or *phenyl* do not become free, but remain in their sphere of attraction.

If benzoyl peroxide is heated[6] in a bomb at 180°, there is a 39 percent yield of diphenyl and gases, of which 80 percent is carbon dioxide. Dietrich[12] noted the formation of diphenyl, explosively, when heated above 144°. In such a change, solvents such as paraffin, nitrobenzene, phenol, cymene or anisole are unattacked, but aniline becomes oxidized to aniline black. The reaction proceeds either in the presence or absence of solvents or of pressure. By employing an apparatus that removes diphenyl constantly,[13] a 68 percent yield of diphenyl may be realized from benzoyl peroxide at 300°. There is some resinification,

[8] Gilman and Adams, *J. Am. Chem. Soc.* **47**, 2819 (1925).
[9] Brunner, *Helv. Chim. Acta* **8**, 651 (1925).
[10] Erlenmeyer, *Helv. Chim. Acta* **8**, 792 (1925).
[11] Fichter and Erlenmeyer, *ibid.* **9**, 144 (1926).
[12] Dietrich, *ibid.* **8**, 149 (1925).
[13] Reynhart,, *Rec. trav. chim.* **46**, 68 (1927).

but there is no evidence for Wieland's view that free radicals play a part in the change. If the reaction is carried out at 210° in bromine vapor, there is no phenyl bromide formed. The suggested mechanism for the pyrolysis is:

$$\begin{matrix} C_6H_5{-}CO{-}O \\ | \\ C_6H_5{-}CO{-}O \end{matrix} \longrightarrow \begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix} + 2CO_2.$$

With Reynhart's apparatus, it was possible to obtain a 92 percent yield of adipic acid and a 98 percent yield of carbon dioxide from succinyl peroxide at 280°.

When benzoyl peroxide (30 percent) is boiled [14] in benzene, carbon dioxide is liberated but no oxygen. These investigators assume a preliminary decomposition of the peroxide into carbon dioxide and the phenyl and benzoate radicals:

$$(C_6H_5CO{-}O)_2 \longrightarrow CO_2 + [C_6H_5{-}CO{-}O{-}] + [C_6H_5{-}].$$

The radicals then react with the benzene (solvent) to form benzoic acid (77 percent yield) and diphenyl, and simultaneously in another fashion to give some phenyl benzoate and benzene. A similar decomposition of di-*p*-chlorobenzoyl peroxide in boiling benzene gives only a monosubstituted diphenyl, which is evidence against Lippman's [15] equation:

$$(PhCO{-}O)_2 \longrightarrow 2CO_2 + Ph{-}Ph.$$

Gelissen and Hermans catalog the reactions of the diacyl peroxides under four headings.

1. *Pyrolysis* of $(R{-}CO{-}O)_2$ into $2CO_2 + R_2$. This occurs when the peroxide is heated alone, or in a solvent above the melting point.

2. *Reaction with the solvent, RH.*

$$\begin{matrix} R{-}CO{-}O \\ | \\ R{-}CO{-}O \end{matrix} + HR' \begin{cases} \longrightarrow R{-}CO_2H + RR' + CO_2 \\ \longrightarrow R{-}CO_2R' + RH + CO_2 \end{cases}$$

3. *Reduction* of $(R{-}CO{-}O)_2$ to $2R{-}CO_2H$, by 2H or by R_2NH, etc.

4. *As acid anhydrides:* $(R{-}CO{-}O)_2 + R'NH_2$ (or H_2O) $\longrightarrow$ $R{-}CO{-}O_2H + R'{-}NH{-}COR$ (or $R'{-}CO_2H$).

In commenting on these reactions, Erlenmeyer [16] has recently stated that dibenzoyl peroxide appears to undergo pyrolysis in two directions. Either it detaches oxygen, with the formation of benzoic anhydride according to him; or, because of superheating, it decomposes according to the Kolbe reaction into diphenyl and carbon dioxide.

Perbenzoic acid, $C_6H_5{-}CO{-}O_2H$, has been found by Erlenmeyer

[14] Gelissen and Hermans, *Ber.* **58**, 285 (1925); **59**, 662 (1926).
[15] Lippman, *Monatsh.* **7**, 375 (1896).
[16] Erlenmeyer, *Helv. Chim. Acta* **10**, 620 (1927).

to decompose with an explosion into oxygen and benzoic acid, by warming. Perpropionic acid, $CH_3CH_2CO_3H$, is much more stable [6] than peracetic acid. The gaseous mixture, formed when perpropionic acid is heated in a steel autoclave, has the following volumetric composition: carbon dioxide, 58.6 percent; ethane, 21.2 percent; methane, 11.0 percent; ethylene, 7.5 percent. Fichter and Reeb [17] have studied the thermal decomposition of perbutyric acid.

[17] Fichter and Reeb, *Helv. Chim. Acta* **6**, 450 (1923).

CHAPTER 10.

ALDEHYDES, AMMONO-ALDEHYDES AND KETONES.

Aldehydes.

Formaldehyde.

One of the characteristic reactions of formaldehyde is that of polymerization. Even at — 20°, liquid formaldehyde polymerizes [1] rapidly to a white solid. At elevated temperatures, depolymerization occurs (see p. 749). At all temperatures between 400-1125°, formaldehyde [2] decomposes suddenly and almost exclusively into hydrogen and carbon monoxide, with no separation of carbon. The pyrolysis above 500° is very rapid and irreversible, but never quite complete. By passing the undiluted vapor over a hot surface of unglazed porcelain, some condensation products are formed, which subsequently change into gaseous products. In one such experiment at 475°, the gases analyzed as follows: carbon monoxide, 44.9 percent; hydrogen, 24.7 percent; carbon dioxide, 19.35 percent; paraffins, 11.05 percent, and some water. At 800°, through an empty tube, or at 650° over iron, formaldehyde breaks down [3] into carbon monoxide and hydrogen, and only traces of methane.

Acetaldehyde.

Acetaldehyde has already been mentioned as a prominent pyrolytic product of ethylene oxide, alcohol, ether and of glycol. Metaldehyde, a polymerization product, is completely depolymerized [4] in a sealed tube at 200°. At high temperatures it undergoes the same type of pyrolysis as acetaldehyde.

The dominant reaction in the decomposition of acetaldehyde is a simple scission into methane and carbon monoxide. At 400°, it [5] is the exclusive reaction:

$$CH_3—CHO \longrightarrow CH_4 + CO,$$

but at 600° secondary reactions appear, since carbon and hydrogen are to be found in the products. A hot porous clay surface tends to induce

[1] Kekulé, *Ber.* 25, 2435 (1892).
[2] Bone and Smith, *J. Chem. Soc.* 87, 910 (1905).
[3] Gautier, *Compt. rend.* 150, 1725 (1910).
[4] Burstyn, *Monatsh.* 23, 737 (1902); Peytral, *Bull. soc. chim.* 27, 34 (1920).
[5] Bone and Smith, *J. Chem. Soc.* 87, 910 (1905).

the vapors of undiluted acetaldehyde to undergo the aldol condensation to water and crotonaldehyde. Somewhat over 13 liters of gaseous products are formed by passing 19.5 cc. of acetaldehyde [6] over pumice at 590-600° during 2 hours. This gas is 50.08 percent methane, 47.5 percent carbon monoxide, and 2.42 percent hydrogen. Traces of unchanged acetaldehyde, of crotonaldehyde and of ethylene may also be recognized. At 1150°, through a small platinum tube,[7] much the same is true. The conversion into methane and carbon monoxide is decidedly the major reaction and that to ethylene, hydrogen and carbon monoxide is secondary. The contact time at this high temperature did not permit of many secondary effects, but a small amount of benzene was identified, showing that the ethylene in part pyrolyzed further to acetylene or to butadiene (see p. 60). The possible formation of ketene [8] and hydrogen from acetaldehyde is mentioned and discussed by Lazier and Adkins, and this has been made the subject of a patent by Dreyfus.

It has recently been demonstrated [9] that the thermal decomposition of gaseous acetaldehyde between 430-592° is homogeneous and bimolecular. Hydrogen iodide, nitrous oxide, hypochlorous anhydride, ozone, and acetaldehyde usually decompose bimolecularly,[10] whereas nitrogen pentoxide, thionyl chloride, dimethyl ether, diethyl ether, acetone and propionaldehyde decompose in a "quasi-unimolecular" way. For acetaldehyde, the heat of reaction for 2 gram-molecules is 45,500 calories. The rate of reaction, k, expressed in gram-mols per liter per second is

$$k = 5.5 \times 10^{10} \sqrt{T} \times e^{-45{,}500/RT}.$$

The pyrolysis of acetaldehyde conforms to the rule that the region of temperature in which a bimolecular reaction attains a given rate is determined by the magnitude of its heat of activation. Other specific factors can apparently play but a minor part in determining the rate of reaction.

Propionaldehyde.

If this aldehyde behaved towards heat like its lower homolog, one would expect a pyrolysis into carbon monoxide and ethane, and this is what has been observed. However, at the temperature of the reaction there are more secondary reactions, because ethane is a less stable com-

[6] Nef, *Ann.* **318**, 198 (1901).
[7] Peytral, *Bull. soc. chim.* **27**, 34 (1920).
[8] Lazier and Adkins, *J. Phys. Chem.* **30**, 898 (1926). Dreyfus, Brit. Pat. 273,810, June 26, 1925; *Chem. Abstracts* **22**, 1981 (1928).
[9] Hinshelwood and Hutchison, *Proc. Roy. Soc.* (London) **111A**, 380 (1926); Hinshelwood, *Chem. Reviews* **3**, 227 (1926).
[10] Hinshelwood, *Proc. Roy. Soc.* (London) **114A**, 84 (1927).

pound than methane, the product from acetaldehyde. If propionaldehyde[6] is passed over pumice at 580-600° at a rate of 1 gram in 10 minutes, a 26 percent yield of ethylene is formed. Also, 10 liters of other gases are formed from 13.8 grams of the aldehyde. This gas is composed of 48.55 percent carbon monoxide, 17 percent ethane, 17.85 percent hydrogen, and 16.6 percent methane. As with acetaldehyde, there are formed traces of other products, namely, acetaldehyde and crotonaldehyde.

As has been indicated, this decomposition[11] of propionaldehyde is apparently unimolecular, at least between temperatures of 449-604° and above pressures of 100 mm. Powdered silica, as a contact agent, does not change the course of the reaction more than 1 percent. The gaseous products at 547° analyze as follows: carbon monoxide, 41 percent; ethane, 26 percent; methane, 19 percent; carbon monoxide and ethylene, 2 percent; and the remainder apparently hydrogen. At higher temperatures, the methane content increases. Hinshelwood suggests that unimolecular reactions are mainly confined to molecules with large numbers of internal degrees of freedom. Propionaldehyde, for example, must have 12 or 14 degrees of freedom to account for the data.

ISOBUTYRALDEHYDE.

Carbon monoxide again represents[6] about half of the gaseous products, after unsaturated hydrocarbons have been removed, when *iso*butyraldehyde (38 grams) is passed over pumice in 1.5 hours at 580-590°. In all, 26 liters of gases are formed with the following composition: carbon monoxide, 47.8 percent; hydrogen, 23.5 percent; methane, 16.9 percent; and ethane, 11.8 percent. The olefine bromides (68 grams) are composed of about equal parts of ethylene and propylene bromides, with a very small amount of divinyltetrabromide (0.25 gram). Also, there is evidence of the formation of a little water, about 0.7 cc. of an oil with the odor of crotonaldehyde, and perhaps a little acetaldehyde.

In a similar investigation with *isovaleraldehyde* (25 grams in 1.5 hours, for the most part at 560-570°), Nef obtained 25 grams of olefine bromides (ethylene, propylene and butylene), 13 liters of other gases, slight evidence of aldehydes, and 1.25 cc. of liquids which were removed by preliminary condensation. The gases are: carbon monoxide, 46 percent; methane, 43 percent; hydrogen, 7.4 percent; and ethane, 3.6 percent. Since *iso*butane is the paraffin which would be anticipated by a simple scission of carbon monoxide, it is interesting to recall the

[11] Hinshelwood and Thompson, *Proc. Roy. Soc.* (London) **113A**, 221 (1926).

behavior of this hydrocarbon towards heat (p. 67). To obtain a better fractionation of the olefine bromides, Nef conducted a simultaneous experiment (44.8 grams in 3 hours at 590-620°) and obtained, by reaction with sulfuric acid, 6.5 cc. of polymerized butylenes and 1.25 cc. of *iso*propyl alcohol (indicating propylene). Also, he obtained 21.8 grams of bromides of other olefines, half of which boiled at 133-136° and the remainder at 136-140°.

Triphenyl-acetaldehyde and Cinnamic Aldehyde

If triphenyl-acetaldehyde is pyrolyzed,[12] the decomposition proceeds in the normal manner to produce carbon monoxide and triphenyl-methane. Should cinnamic aldehyde also follow this general reaction, then the major products of the reaction would be carbon monoxide and styrene:

$$C_6H_5—CH=CH—CHO \longrightarrow CO + C_6H_5—CH=CH_2.$$

When the vapors[13] of this aldehyde are passed rapidly through a hot tube, this is found to be the chief reaction and proceeds to the extent of about 27 percent. The styrene suffers further decomposition, to a certain extent into benzene and acetylene. Some of the acetylene reacts with hydrogen, another by-product, to produce ethylene. The liquid reaction products are benzene, styrene, unchanged aldehyde, and some distyrene. The gaseous products represent 11.4 percent of the aldehyde. By volume, they are 73 percent carbon monoxide, 9 percent hydrogen, 3.1 percent benzene, 3.6 percent ethylene, 8.7 percent acetylene, and 2.6 percent methane.

Benzaldehyde.

Benzaldehyde is the only simple aromatic aldehyde that has been extensively studied. Its mode of decomposition varies decidedly with the circumstances. In the vapor phase, at sufficiently high temperatures, the simple decomposition into carbon monoxide and benzene is almost the exclusive primary reaction:

$$C_6H_5CHO \longrightarrow CO + C_6H_6.$$

With a sealed tube reaction at about 350°, the change is almost exclusively in the direction of the Cannizzaro reaction, giving benzyl benzoate:

$$2C_6H_5CHO \longrightarrow C_6H_5CO—O—CH_2C_6H_5.$$

[12] Orekhoff and Tiffeneau, *Compt. rend.* **182**, 67 (1926).
[13] Peytral, *Bull. soc. chim.* **39**, 214 (1926).

Metallic catalysts, such as reduced nickel, appear to assist [14] the elimination of carbon monoxide from aldehydes; with benzaldehyde, the conversion into pure carbon monoxide and benzene takes place at 220°, and with furfural, at 270°. The condensation of aldehydes to esters is especially catalyzed by aluminum ethoxide, particularly in the presence of zinc chloride as a promoter.[15] This is the Tischtschenko reaction.

Peytral [16] has subjected the vapors of benzaldehyde to a temperature of 1150° in an 11 cm. platinum tube. Similar results have recently been obtained in the author's laboratory [17] at about 690° in a Pyrex tube about 30 cm. long. The longer contact time in the latter case is compensated by the lower temperature. Mlle. Peytral observed not only benzene and carbon monoxide, but also some diphenyl and hydrogen due to the further pyrolysis of the benzene. A small quantity of methane and carbon are also formed. One observation of Mlle. Peytral's has been shown to be a misleading one. She obtained a little crystalline material of melting point 213°, which was stated, without further proof, to be anthracene. This was also obtained by Hurd and Bennett, but it was demonstrated that it could not be anthracene since it failed to form a picrate, and since it could not be oxidized to anthraquinone. It was definitely identified as *p*-diphenylbenzene, $C_6H_5—C_6H_4—C_6H_5$. This is the compound which one would expect inasmuch as it is known to be formed from benzene.

In Hurd and Bennett's work, benzaldehyde was passed through a hot tube (680-690°), originally filled with nitrogen. Forty-one grams was passed during 4 hours; this gave 31 grams of distillate and 5.8 liters of gas, calculated to standard conditions. By fractionation, the distillate gave 13.5 grams of unchanged benzaldehyde, 11 grams of benzene, 2.5 grams of diphenyl and 0.3-0.5 gram of *p*-diphenylbenzene. The gaseous portion contained no methane or unsaturated hydrocarbons, but gave the following analysis, by volume: carbon monoxide, 86.7 percent; hydrogen, 12.9 percent; carbon dioxide, 0.32 percent. The calculated weights of these three gases, respectively, would therefore be 6.20 grams, 0.0062 gram, and 0.02 gram. The absence of methane is at variance with Peytral's work, although the conditions of the reaction are not the same.

Benzaldehyde is not appreciably decomposed [18] in a sealed tube at 250°, even after an 18-hour period. In fact, Hurd and Bennett could

[14] Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co., 1922, paragraph 618.
[15] *See* Child and Adkins, *J. Am. Chem. Soc.* **47**, 798 (1925).
[16] Peytral, *Bull. soc. chim.* **29**, 44 (1921).
[17] Hurd and Bennett, unpublished results.
[18] Lachman, *J. Am. Chem. Soc.* **46**, 720 (1924).

find almost no change in 2 hours at 300-310°, but this is contrary to Lachman's finding a 30 percent conversion into benzyl benzoate under these conditions. For a 30 percent pyrolysis of the benzaldehyde, Hurd and Bennett required a 2 hours' heating at 350-370°. With a 15-hour run at 300°, Lachman reported an 80 percent change.

With Lachman's 2-hour run, the data show that almost no gaseous products are formed, and that 35 grams from the original 50 grams of benzaldehyde may be recovered. After removal of the benzaldehyde, one-third of the residue is benzoic acid (4 grams), which may be removed by cold, very dilute sodium hydroxide solution, thereby leaving 8 grams of liquids, 7 grams of which boil under 5 mm. at 130-160°. The latter is chiefly benzyl benzoate. Lachman reported 2 grams of toluene as a reaction product, but Hurd and Bennett could find no evidence of this. Instead, it seems reasonable to assume that much of this "toluene" may have been benzene; in such an event, the "slight pressure" may have been due to carbon monoxide. In the 15-hour run, the effects of this reaction undoubtedly accumulated, for "there was much pressure in the tube". In Hurd and Bennett's 2-hour run [17] at 350-370°, considerable pressure was apparent in the tube after cooling over night. About 43 grams of benzaldehyde, from an original 62.5 grams, was recovered. A 2-gram sample of distillate of boiling point 70-120° was converted into a dinitro derivative, which was unquestionably dinitrobenzene. Possibly a nitro-toluene may have been present, but if so it was in amounts too small to identify. The other products of the pyrolysis were 0.5 gram of benzoic acid, and 15.5 grams of benzyl benzoate. In confirmation of the latter statement, it was found that 15 grams of the ester gave 8.4 grams of benzoic acid and 7 grams of benzyl alcohol on saponification. It will be noticed that the quantity of benzoic acid which was formed prior to the hydrolysis is not comparable in the two experiments (4 grams from 50 grams, as contrasted with 0.5 gram from 62.5 grams). Hurd and Bennett demonstrated conclusively that stilbene and phenanthrene are not products of the pyrolysis of benzaldehyde, and it will be shown later that they are not formed in the pyrolysis of benzyl benzoate. Neither stilbene nor phenanthrene were mentioned by Lachman; but in one other detail, the results of Lachman are at variance with those of Hurd and Bennett. In both cases, the benzyl benzoate, which was formed as a product of pyrolysis, was subjected to hydrolysis by means of alcoholic potassium (or sodium) hydroxide. Hurd and Bennett found the anticipated products of benzyl alcohol and benzoic acid, as has been stated. Lachman, however, reported dibenzyl ether (7 grams of the ester gave 1.5

grams of benzoic acid, 1 gram of benzyl alcohol, and 3 grams of dibenzyl ether). No evidence except the boiling point (135-137° at 5 mm.) was given in proof of the statement; furthermore, Hurd and Bennett could not check the observation. Lachman's explanation of the presence of dibenzyl ether is particularly flimsy. He suggests that it came from the benzyl alcohol by superheating, but since there was no benzyl alcohol until after the hydrolysis it is difficult to see how it could have been superheated in a few minutes at 80-160°, when Lachman [19] himself showed (p. 156) that benzyl alcohol pyrolyzed in 5 days at 210-215°. Also, it is difficult to see why the benzoic acid content from the ester should be small in comparison to the combined content of benzyl alcohol and "dibenzyl ether". Lachman showed that benzoin and benzil were definitely absent in the reaction products of benzaldehyde.

In recapitulation, the chief reaction product of benzaldehyde in a sealed tube at 350-370° is benzyl benzoate, and most of this escapes further pyrolysis. About two-thirds of the benzaldehyde is unchanged, but some of it also undergoes a simple decomposition into carbon monoxide and benzene. This reaction becomes pronounced at high temperatures.

Hydroxy-aldehydes.

Glycollic aldehyde, $CH_2OH—CHO$, apparently undergoes [20] a polymerization process by heating in a vacuum for several hours at 100°. At least, the viscous reaction product is sweet-tasting. It still reduces Fehling solution, and gives rise to a "hexose" osazone.

$$3CH_2OH—CHO \longrightarrow CH_2OH—(CHOH)_4—CHO.$$

Recently, it has been observed [21] that dry distillation of glycollic aldehyde, tartaric acid, arabinose, sucrose, starch, or filter paper all yield products, which, after steam distillation, give a scarlet colored nickel dioximine, indicating diacetyl.

The homolog of glycollic aldehyde, lactaldehyde,[22] rearranges somewhat, although in undetermined amount, into acetol by distillation:

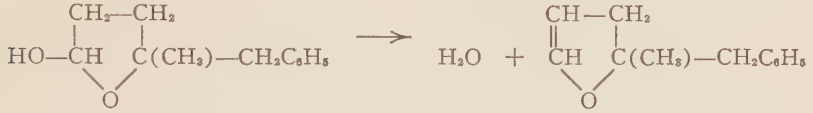
$$CH_3—CHOH—CHO \longrightarrow CH_3—CO—CH_2OH.$$

Certainly, much of the aldehyde is not changed if small quantities are used in the distillation, but there is resinification when large amounts are treated.

[19] Lachman, *J. Am. Chem. Soc.* **45**, 2358 (1923).
[20] Fenton, *J. Chem. Soc.* 67, 779 (1895); 71, 375 (1897).
[21] Schmalfuss and Barthmeyer, *Ber.* 60, 1035 (1927).
[22] Wohl and Lange, *Ber.* **41**, 3609 (1908).

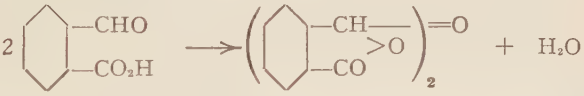
The β-hydroxyaldehydes, or *aldols*, have been discussed on pp. 164-5.

Gamma-hydroxyaldehydes exist largely in the lactonic form.[23] For example, γ-hydroxy-γ-methyl-caproic-aldehyde is in reality 2-methyl-2-ethyl-5-hydroxytetrahydrofurane. Many compounds such as this may be distilled in a vacuum, but with the 2-benzyl derivative, water is eliminated even at 3.6 mm. (bath temperature, 180-190°).



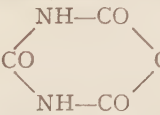
The lactone structure is common also in *delta*-hydroxyaldehydes, and as is well known, these butylene- and amylene-oxide rings are commonly encountered in the carbohydrates.

Dehydration in the following aldehyde-acid occurs [24] at 250°:



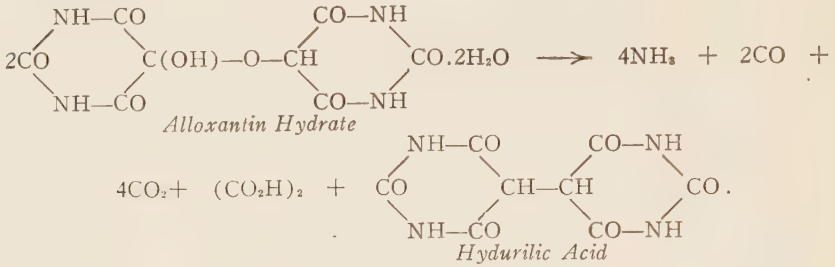
CARBONYL DERIVATIVES, OF THE TYPE $=C\begin{matrix}OH\\X\end{matrix}$.

Perhaps the best known compound illustrative of the $=C(OH)_2$ grouping is chloral hydrate, $CCl_3—CH(OH)_2$. Vapor density determinations on the vapors of boiling chloral hydrate (96-98°) show dissociation [25] into chloral and water. The molecule of water attached to glyoxylic acid, $HO_2C—CH(OH)_2$, cannot be eliminated by heat.[26] Above the melting point of the compound, there is a partial decomposition into oxalic and glycollic acids. Not much carbon dioxide is evolved, but at slightly higher temperatures carbon dioxide is evolved freely. The residue becomes darker in color, but yields no distillate. Water is not liberated, and the compound is completely destroyed.

The hydrates of alloxan,  , and of *N,N*-dimethyl-alloxan, behave similarly, although in a high vacuum dehydration [27] is possible at 200-220°. Alloxantin [28] loses its two molecules of

[23] Helferich and Gehrke, *Ber.* **54**, 2640 (1921). *See also* p. 229.
[24] Graebe and Truempy, *Ber.* **31**, 371 (1898).
[25] Dumas, *Ann. chim. phys.* [2] **56**, 136 (1834); Fluckinger, *Jahresbericht der Chemie*, 1870, 611.
[26] Debus, *J. Chem. Soc.* **85**, 1391 (1904); *Ann.* **338**, 336 (1905).
[27] Biltz, *Ber.* **45**, 3659 (1912).
[28] Hlasiwetz, *Ann.* **103**, 216 (1857); Murdock and Doebner, *Ber.* 9, 1102 (1876).

water at 150°. The hydrate undergoes a deep-seated decomposition at 170° in a sealed tube:



The hydrate of benzoyl-formaldehyde, $C_6H_5CO—CH(OH)_2$, melts [29] at 73°. By heating it above its melting point, water is driven off, and at higher temperatures, the anhydrous aldehyde distils (boiling point (125 mm.) 142°). Another compound which appears to possess the dihydroxy-methane configuration is mesoxalic acid. The ethyl ester of mesoxalic acid absorbs water from the air to form the crystalline compound, $C_2H_5O_2C—C(OH)_2—CO_2C_2H_5$, which decomposes somewhat into the anhydrous ester on distillation.

In general, hemi-acetals are unstable. The hemi-acetal of monochloroacetaldehyde [30] is isolable, but at the boiling point, 95°, it undergoes a disproportionation into chloroacetaldehyde (81 percent yield) and its diethyl acetal (92 percent yield):

$$2CH_2Cl—CH\begin{matrix}OH\\OEt\end{matrix} \longrightarrow H_2O + CH_2Cl—CHO + CH_2Cl—CH(OC_2H_5)_2.$$

For acetals, see pp. 229, 271.

*Iso*cyanate derivatives of this type, $RHC\begin{matrix}OH\\NCO\end{matrix}$, decompose [31] at once into the aldehyde. In the presence of alcohol, the liberated *iso*-cyanic acid forms ethyl allophonate. As might be expected, the derivatives, $RHC\begin{matrix}OR\\NCO\end{matrix}$, are stable. Substances with the structures $=CCl—OH$ are also usually unstable, but dicinnamenyl chlorocarbinol [32] possesses a rather unusual degree of stability. If heated for 45 minutes in a vacuum at 60° after there is no longer any visible reaction, there results a 27 percent yield of the anhydride of the original compound.

[29] von Pechmann, *Ber.* **20**, 2905 (1887).
[30] Fritsch and Schumacher, *Ann.* **279**, 305 (1894).
[31] Jones and Powers, *J. Am. Chem. Soc.* **46**, 2519 (1924).
[32] Straus and Caspari, *Ber.* **40**, 2701 (1907).

The di-*p*-chlorocinnamenyl chlorocarbinol behaves similarly. It pyrolyzes stormily at 95-100°, giving 10-15 percent yields of anhydride.

$$2(C_6H_5CH{=}CH)_2C{<}\begin{matrix}OH\\Cl\end{matrix} \longrightarrow H_2O + ((C_6H_5CH{=}CH)_2CCl)_2O.$$

The $=C{<}\begin{matrix}OH\\NH_2\end{matrix}$ configuration is the primary result of the reaction between aldehydes and ammonia. Ordinary aldehyde ammonias, however, do not preserve this arrangement, but instead polymerize into heterocyclic structures. The $=C(OH)—NH_2$ group is stabilized by the presence of strongly negative substituents. Urea, $HN{=}C{<}\begin{matrix}OH\\NH_2\end{matrix}$, and the ammonia derivative of chloral, $CCl_3—CH(OH)—NH_2$, are examples of this. Urea will be studied in detail in a later chapter.

It has been found recently that acetone reacts with liquid ammonia [32a] at −65°, giving a crystalline addition product, $(CH_3)_2C{<}\begin{matrix}OH\\NH_2\end{matrix}$, which melts at −41°. Above the melting point, the compound decomposes into acetone and ammonia.

Carbon monoxide diethyl acetal [33] is a compound of recent interest. It boils at 77°, but in so doing suffers a slow decomposition into carbon monoxide and diethyl ether:

$$C(OC_2H_5)_2 \longrightarrow CO + (C_2H_5)_2O.$$

Ammono-aldehydes.

Hydrobenzamide is the reaction product of benzaldehyde and ammonia, and in Professor E. C. Franklin's terminology it is an aldehyde of the ammonia system. When hydrobenzamide [34] is maintained at 130° for 3-4 hours, it gives good yields of amarine. Strain [35] has remarked that this reaction "is entirely analogous to the formation of benzoin from benzaldehyde, as the following equations indicate":

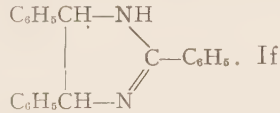
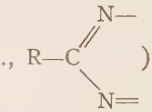
$$\begin{matrix}C_6H_5CH{=}O\\+\\C_6H_5CH{=}O\end{matrix} \longrightarrow \begin{matrix}C_6H_5CH{—}OH\\|\\C_6H_5C{=}O\end{matrix}$$

Benzaldehyde — *Benzoin*

$$\begin{matrix}C_6H_5CH{=}N\\>CHC_6H_5\\C_6H_5CH{=}N\end{matrix} \longrightarrow \begin{matrix}C_6H_5CH{—}NH\\|\quad\quad>CHC_6H_5\\C_6H_5C{=}{=}N\end{matrix}$$

Hydrobenzamide — *Amarine Isomer*

[32a] Hock and Stuhlmann, *Ber.* **61**, 470 (1928).
[33] Scheibler, *Ber.* **59**, 1022 (1926).
[34] Bertagnini, *Ann.* **88**, 127 (1953); Bahrmann, *J. prakt. Chem.* [2] **27**, 296 (1883).
[35] Strain, *J. Am. Chem. Soc.* **49**, 1565 (1927).

It should be pointed out in criticism that although the two equations appear to be analogous, the method of bringing about these two reactions is quite different. There seems to be absolutely no trace of benzoin formed from benzaldehyde by simple heating. Instead, the reaction is of the Cannizzaro type, leading to benzyl benzoate. As Strain points out, to explain the existence of *d, l,* racemic and *meso* forms of amarine, the above formula for amarine (named amarine isomer) cannot be truly representative of fact, and that the structural formula of amarine must be  . If the latter formula is examined, it will be seen that the two adjacent cyclic carbon atoms are of the ammono-alcoholic type (i.e., $R_2CH—N=$), whereas the other carbon atom in the ring is definitely related to an ammono-acid (i.e., ). This is precisely the situation which is encountered in benzyl benzoate. Exclusive of phenyl groups, one carbon atom is related to benzyl alcohol, whereas the other is related to benzoic acid. Thus, it seems established that benzaldehyde and "ammono-benzaldehyde" both undergo pyrolysis according to a common mechanism at fairly low temperatures, giving a reaction of the Cannizzaro type. The high-temperature decomposition of benzaldehyde leads to benzene and carbon monoxide, instead of benzyl benzoate; so also, the high-temperature decomposition of hydrobenzamide may be found to follow quite a different course from that which has just been outlined.

Dibenzylidene-*o*-phenylene diamine gradually changes[36] above its melting point, 106°, into benzaldehydine:

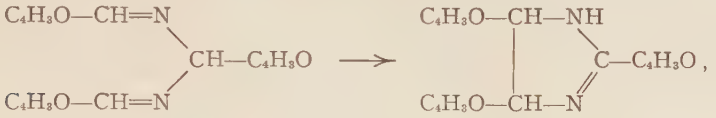
The former compound is an excellent illustration of an "ammono-aldehyde" related to benzaldehyde, and the course of reaction parallels the change of benzaldehyde into benzyl benzoate.

The two asymmetric atoms in amarine may be regarded as internally compensated (meso). Conversion into the racemic "*iso*amarine" is effected by maintaining amarine hydrochloride above its melting point for a short time. *Iso*amarine is also formed, together with lophine and

[36] Hinsberg and Koller, *Ber.* 29, 1497 (1896).

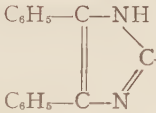
tetraphenyl-pyrazine, when the substance, $C_6H_5CH{=}N{-}CH(C_6H_5){-}CN$, is heated [37] to 215°.

The conversion of hydrobenzamide into amarine has a parallel [38] in the change of furfuramide to furfurine. This rearrangement:



occurs in 30 minutes at 110-120°, but only in 10 percent yields, and during the process there is an intense blackening. To prepare furfurine, it was recommended instead to reflux furfuramide in a dilute solution of potassium hydroxide.

At high temperatures, hydrobenzamide,[39] or amarine,[40] or *iso*-amarine [37] all lose two atoms of hydrogen and generate lophine,[41] or triphenyl-glyoxaline:



which distils undecomposed. Hydrobenzamide first melts to a yellow liquid; further heating deepens the color to orange, and at 360° it decomposes stormily.[42] The yield of pure lophine represents about one-third of the amount of benzaldehyde taken originally to prepare the hydrobenzamide. Much ammonia and hydrogen are evolved, as well as toluene, benzonitrile and stilbene. The weight of toluene formed is one-tenth that of the lophine.

A quantitative yield [43] of lophine sublimes when a monosilver salt of amarine is heated above its melting point (218°). Presumably, hydrogen is also evolved, for a residue of pure silver is left. Lophine is of unusual interest because of the fact that a solution of it in alcoholic potassium hydroxide emits light as it absorbs oxygen at 65°.

Two molecules of acrolein interact with one of ammonia [44] to form a compound, C_6H_9ON, and water. This substance changes into picolin by loss of a molecule of water as it is dry distilled.

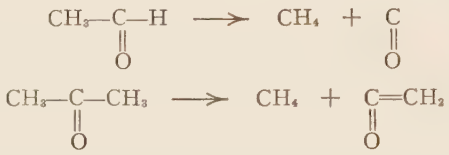
Ketones.

Acetone.

Aldehydes and ketones have so many points in common that it is fair to ask if there may be a similarity in the pyrolysis of members of

[37] Snape and Brooke, *J. Chem. Soc.* **71**, 529 (1897).
[38] Bahrmann, *loc. cit.*
[39] Laurent, *Ann.* **21**, 130 (1837); **52**, 359 (1844).
[40] Fownes, *Ann.* **54**, 368 (1845).
[41] For the structure of lophine, *see* Strain, *J. Am. Chem. Soc.* **49**, 1566 (1927).
[42] Radziszewski, *Ber.* **10**, 71 (1877); Pinner, *Ber.* **35**, 4140 (1902).
[43] Claus and Elbs, *Ber.* **16**, 1272 (1883); Claus and Kohlstock, *Ber.* 18, 1850 (1885).
[44] Claus, *Ann.* **130**, 185 (1864); **158**, 222 (1871).

the two systems. If acetaldehyde and acetone are selected as representative members, it would seem that there is a decided similarity since both substances break down in a simple manner at higher temperatures with methane as a common product:



Carbon monoxide, from the aldehyde, and ketene, from the ketone, have rather obvious structural points of similarity.

The pyrogenic decomposition of acetone has attracted a number of investigators. Several years ago, Barbier and Roux [45] passed acetone vapor through a copper tube of one meter length, and reported an almost quantitative reaction at 1000° in accordance with the equation:

$$2CH_3COCH_3 \longrightarrow 2CH_4 + 2CO + C_2H_4.$$

Some of the ethylene decomposed further at the high temperature with the resultant formation of acetylene, hydrogen (and methane).

In 1901, Nef [46] described an experiment in which 30 grams of acetone was passed over pumice at 530-580° during 80 minutes. There was collected 11.7 grams (14.5 cc.) of distillate, 11.5 cc. of which was unchanged acetone; the remainder boiled between 65-110°, and was thought to contain crotonaldehyde and some acetaldehyde (see p. 19). Very probably, the odor which Nef thought to be due to these two aldehydes was caused by ketene, but at this time ketene had not been discovered. Fifty-four grams of pure ethylene bromide and 14 liters of gas were the chief observed products of the reaction. An analysis of a sample of the last 10 liters of gas was as follows: *pure* methane 53.25 percent, carbon monoxide 38.15 percent, hydrogen 8.6 percent.

The first investigators to list ketene, $CH_2{=}C{=}O$, as a pyrogenic product were Schmidlin and Bergman.[47] According to their method, acetone is passed through a combustion tube, filled with pieces of clay, which is heated to 500-600°. Two-thirds of the acetone pyrolyzes to form ketene; the remainder is condensed in a series of 6 bottles, filled with glass wool, and cooled by an ice-salt mixture. About 23 percent of the total yield of ketene was found to be dissolved in this distillate. The yield of "available ketene" which is not absorbed by the acetone

[45] Barbier and Roux, *Bull. soc. chim.* [2] **46**, 268 (1886).
[46] Nef, *Ann.* **318**, 191 (1901).
[47] Schmidlin and Bergman, *Ber.* **43**, 2821 (1910).

in these bottles is slightly less than 11 percent. This yield is based on the unrecovered acetone.

Peytral,[48] working at 1150° (short platinum tube), reached the conclusion that there is but one primary reaction when acetone is pyrogenically decomposed, namely, the pyrolysis into ketene and methane. Ketene, in turn, may then be broken further into ethylene and carbon monoxide. She also noticed a very small amount of acetaldehyde. Her data follow for four experiments.

TABLE XXVI. *Pyrolysis of Acetone.*

	I	II	III	IV
Duration of experiment, in seconds	32	38	52	25
Weight of acetone used, in milligrams	592	1032	1787	1187
Milligram-mols per second	0.55	0.63	0.76	1.00
Weight of acetone condensed, in milligrams	5	297	741	520
Weight of aldehyde in distillate, in milligrams	..	..	8	2
Weight of other aldehyde, in milligrams	..	4	8	4
Cubic centimeters of gases (standard conditions)	510	442	598	278
Composition of gases		Percent		
Methane	36.6	45.6	46.3	54.4
Carbon monoxide	38.0	37.4	35.1	30.1
Ethylene	13.5	14.4	14.9	13.4
Hydrogen	10.5	2.1	3.0	1.6
Acetylene	1.4	0.5	0.7	0.5

The pyrogenic decomposition of acetone into ketene is by far the best synthetic method for ketene. Because of the value of ketene as an acetylating agent, the optimum conditions have been determined[49] for ketene production:

$$CH_3—CO—CH_3 \longrightarrow CH_4 + CH_2=C=O.$$

The heating unit of the apparatus may be either an ordinary combustion furnace or an electrically heated furnace. The apparatus should be designed to separate the ketene from the unused acetone as rapidly as possible to prevent loss of ketene by solution in the acetone. With a given efficient apparatus, the temperature, the rate of flow of acetone and the percentage decomposition of acetone all influence the yield. For practical purposes, the following conditions appear to be best; temperature, 700°; rate of flow of acetone, 5 cc. per minute; decomposition of acetone, between 25-40 percent of that introduced. These conditions give consistent yields of ketene which range between 35-45 percent, some three or four times better than the yield originally reported by Schmidlin and Bergman.

[48] Peytral, *Bull. soc. chim.* [4] **31**, 122 (1921).

[49] Hurd and Cochran, *J. Am. Chem. Soc.* **45**, 515 (1923); Hurd and Tallyn, *ibid.* **47**, 1427 (1925); Hurd, "Organic Syntheses," New York, John Wiley and Sons, 1925, p. 39.

The temperature mentioned above is about 100-200° higher than the temperature first advocated by Schmidlin and Bergman, although it is in close agreement with the temperature, 710°, suggested by Staudinger.[50] The following table lists the data on some representative runs, as obtained by Hurd and Tallyn.

TABLE XXVII. *Pyrolysis of Acetone.*

Temperature °C.	Time Minutes	Cubic Centimeters			Ketene Percent
		Used	Condensed	Decomposed	
630	31	50	39.5	11.5	19.6
665	48	125	104	21	33.2
695	42	81	31	50	32.3
695	25	125	94.5	30.5	45.1
695	26	125	95.5	29.5	45.0
700	20	125	113	12	48.0
705	112	290	240	50	39.7
710	24	125	75	50	38.2
720	56	86.5	34.5	52	30.7
735	16	79	29	50	33.4
735	18	125	76	49	37.0

There is a rough relationship which can be drawn between the percentage of acetone decomposed and the percentage yield of ketene. The reason for it undoubtedly lies in the fact that ketene vapor is prevented from decomposition, once it is formed, by sweeping it rapidly from the furnace with acetone vapor. In the experiments in which over half of the acetone was decomposed, regardless of other factors, the highest yield obtained was 34.4 percent and the highest yield was only 27.4 percent when four-fifths or more of the acetone was decomposed. When less than half, or better yet, when less than 40 percent of the acetone is decomposed, the yields are much better.

The data in the table show that it is sometimes possible to duplicate results to a nicety. However, with a high temperature reaction such as this, it would be astonishing if it could be done consistently, and indeed the greater portion of the data indicate the impossibility of nice duplication. It may be said, however, that most of the results of the experiments carried out under similar conditions are comparable.

A comparison of the first two runs in the table at 695° indicates that the rate of flow of acetone has a bearing on the yield of ketene. In the first run, the rate of flow is 1.9 cc. per minute and in the second 5 cc. per minute. The higher yield in the latter case is due in part to this cause, but also in part to the difference in rate of decomposition of acetone. Here again, no exact numerical relationship can be stated, but in a general way it seems that the best rate of flow is about 5 cc.

[50] Staudinger and Hauser, *Helv. Chim. Acta* 4, 887 (1921).

per minute. Good results have been obtained between 2.5 and 7 cc. per minute.

An attempt to correlate the combined effect of these two factors, namely, the rate of flow of acetone and the rate of decomposition of acetone, was fruitless. The rate of decomposition of acetone appears not to be a factor in the ultimate yield of ketene. This may be interpreted to mean that whatever effect the percentage of undecomposed acetone may have upon the yield of ketene, it is an effect that is independent of the rate of flow of acetone.

There is a relationship, however, between temperature and rate of flow of acetone. Within limits, a higher temperature may be used without seriously diminishing the yield of ketene, provided the flow of acetone is accelerated accordingly. This observation coincides with that of Mlle. Peytral, who noted that when acetone vapors are passed rapidly through a platinum tube 11 cm. long at 1150°, a pronounced ketene odor becomes apparent which is absent when acetone is introduced at a slower rate.

Recent patents[51] describe the preparation of "ketenes" by the thermal decomposition of acetone, acetic anhydride, "or similar compounds", in the presence of metallic sulfates which are not decomposed by heating to 700°. A temperature of about 635° is suggested as the temperature for the conversion. The "catalysts", aluminum sulfate is mentioned particularly, are supposed to function as anti-catalysts, to preserve the ketene at the temperature of the reaction. An approximately quantitative yield is claimed. After trying out one or two of these sulfates, which are supposed to lead to a quantitative yield of ketene, the author cannot look upon the claims of the patent any too optimistically. In some cases, the yields were nil, and in no case was the yield as high as when porcelain was used as filler for the reaction tube. With porcelain, the yield is good, but it is far from quantitative.

No catalysts have been produced as yet for ketene production from acetone. At 270°, over nickel, acetone is rapidly decomposed[52] into methane, carbon monoxide, hydrogen and carbon. Copper has no effect on ketones, at least below 400°. It is possible that a tinned-iron tube would have no catalytic effect, but ordinary, unpolished iron[53] appears to promote the decomposition of acetone, or perhaps of ketene, into methane, carbon and hydrogen. The temperature in the latter case was

[51] Ketoid Co., Brit. Pat. 237,573, July 22, 1924; Nightingale, U. S. Pat. 1,602,699, Oct. 12, 1926; *Chem. Abstracts* **20**, 1415, 3697 (1926).
[52] Sabatier and Senderens, *Ann. chim. phys.* [8] **4**, 474 (1905).
[53] Hurd and Tallyn, *J. Am. Chem. Soc.* **47**, 1427 (1925).

about 600°, and the effect may have been due to the presence of metallic oxides in the pipe. The reaction:

$$CH_2{=}C{=}O \longrightarrow H_2O + 2C,$$

is very probable in this case. Since aluminum oxide is a catalyst for dehydration, it was thought that possibly aluminum carbide might serve as catalyst for demethanation, thereby assisting the liberation of methane from acetone. This [54] has not been found to be the case, however. Almost no ketene was formed in the few cases in which it was put to the test. With regard to the deposition of carbon from the vapor phase of a number of compounds such as acetone, acetic acid, alcohols and some paraffin oils, Tanner [55] has found that iron affords an abundant deposit which indicates that true pyrolysis is very apt not to occur in an apparatus made of iron. Copper does not give this carbon deposit.

By heating acetone under pressure [56] at 500°, carbon, carbon monoxide and other gases are formed, whereas at 350-400° the reactions are largely those of dehydration-condensation. In much of Ipatiew's work, catalysts are also employed.

Hinshelwood [57] has recently published some interesting data to show that the pyrolysis of acetone is a true unimolecular, homogeneous reaction. The reasons advanced are twofold. First, the time necessary for any fraction of the total change to complete itself is independent of the initial pressure; and secondly, it is independent of the amount of surface exposed (silica walls or powder). The products stated by these investigators to be formed are mainly carbon monoxide, methane, hydrogen and some ethylene and carbon dioxide. It is rather curious that no mention was made of the presence of ketene as a reaction product, but instead he postulates the mechanism of scission for acetone into carbon monoxide and two methyls. Taylor [58] has already criticized this feature, and has suggested that possibly Hinshelwood and Hutchison were not actually measuring the rate of pyrolysis of acetone, but of ketene.

The data of Hinshelwood and Hutchison show that at 596°, 119 seconds (average of 6 readings) is the time required for the pressure to increase by 50 percent of the initial pressure, which by the way varied from 190 to 401 mm. The latter value (119 sec.) was determined with an empty quartz bulb; when the bulb was one-third full of silica powder, nearly the same value, 115 seconds, was observed. In the following

[54] Hurd and Martin, unpublished results.
[55] Tanner, University of Oregon, private communication.
[56] Ipatiew and Petrov, *Ber.* **60**, 753, 1956, 2545 (1927).
[57] Hinshelwood and Hutchison, *Proc. Roy. Soc.* (London) **111A**, 245 (1926).
[58] Taylor, *J. Phys. Chem.* **30**, 1433 (1926); book review.

table, t, t′ and t″ are the number of seconds required for the pressure to increase by 25, 50 and 75 percent respectively of the initial value. The data reveal the fact that time and initial pressure are independent.

TABLE XXVIII. *Relation Between Time and Initial Pressure in Pyrolysis of Acetone.*

Temperature °C.	Initial Pressure Millimeters	t	t′	t″
			Seconds	
578	385	100	275	754
	362	91	260	655
	189	92	270	700
	112	103	275	620
601	362	26	77	199
	296	27	80	200
	192	20	78	...
	98	30	86	222

From such time values as these, Hinshelwood derived concordant values of 68,500 calories as the heat of activation of this reaction, for introduction in the equation:

$$\ln k = 34.95 - (68{,}500/RT).$$

The value of k at 534° is 0.00038; and at 578°, is 0.0033.

Other Aliphatic Ketones.

Methylethyl and Diethyl Ketone. The pyrolyses of methylethyl ketone and diethyl ketone [59] have also been studied. These ketones are of interest, since they have the possibility of decomposing into methyl ketene. If the decomposition pursued a similar course to that of acetone, methylethyl ketone could give either ketene or methyl ketene, whereas diethyl ketone could only give methyl ketene as a primary product of decomposition:

$$CH_3—CO—CH_2—CH_3 \begin{cases} \nearrow & CH_2=C=O + C_2H_6 \\ \searrow & CH_4 + CH_3—CH=C=O \end{cases}$$

and

$$C_2H_5—CO—C_2H_5 \longrightarrow CH_3CH=C=O + C_2H_6.$$

Actually, both ketene and methyl ketene were found in the first case, and curiously enough also in the second. Ketene overshadows the methyl ketene in both cases, although more pronouncedly so in the first. The combined yield of both ketenes from methylethyl ketone is about 5 percent, and from diethyl ketone is about 8 percent. In these experiments, the heating was accomplished not only with a combustion furnace, but also with an incandescent platinum filament in a specially designed apparatus.

[59] Hurd and Kocour, *J. Am. Chem. Soc.* **45**, 2167 (1923); Hurd, *ibid.* 3095.

The formation of both ketene and methyl ketene from diethyl ketone points to the fact that methyl ketene must undergo pyrolysis, in part at least, to ketene and ethylene:

$$2CH_3—CH=CO \longrightarrow C_2H_4 + 2CH_2=CO.$$

In spite of the low yield of methyl ketene, this reaction is of interest since methyl ketene has been prepared by only one other method, namely, by the action of zinc shavings on α-bromopropionyl bromide. The yield is also small by this method.

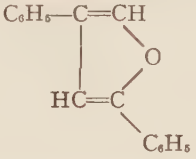
Pinacolone, $(CH_3)_3C—CO—CH_3$, is remarkably stable at 665° (3 cc. per minute), but most of it undergoes pyrolysis [60] into gaseous products at 705° when it is introduced into the furnace at a rate of 1 cc. per minute. Less than 2 percent of ketene is produced. Pinacolone possesses an acetyl group as does acetone. Differing from acetone, however, the tertiary carbon to which it is linked makes it impossible for methane to be eliminated as a primary decomposition product. There was found but little evidence to indicate that it undergoes scission into ketene and *iso*butane (or its products of decomposition), and none whatever that it forms dimethyl ketene and ethane.

From this, it may be inferred that no ketone with the carbonyl group attached to a tertiary carbon will prove suitable for ketene production. This immediately eliminates the aromatic ketones, such, for example, as acetophenone. Other factors, however, may appear; one such is the relative electron attraction of the radical attached to the acetyl group. Methyl is highly electronegative; phenyl is more so, and tertiary butyl is much less so. On this basis, acetophenone and pinacolone would not be comparable. It has already been shown (p. 90) that methyl-β-tetralyl ketone and acetyl-tetraphthene are stable at moderate temperatures, and that at 700°, nuclear hydrogen is detached from the molecule.[61] The acetyl group is stated to be largely unattacked. However, the fact that naphthalene and acenaphthylene are also formed, makes it interesting to speculate as to the fate of the acetyl group. Either it must have been severed ketenically, or it was reduced off by the hydrogen which was simultaneously present.

Acetophenone has been found [62] to decompose into a variety of products by passing it through a red-hot tube. These include benzene, diphenyl and 1,4-diphenylbenzene, of which benzene is undoubtedly the primary product and the other two compounds secondary. The gaseous products include carbon monoxide, methane, hydrogen and small quan-

[60] Hurd and Tallyn, *J. Am. Chem. Soc.* **47**, 1779 (1925).
[61] von Braun, Hahn and Seeman, *Ber.* **55**, 1687 (1922).
[62] Barbier and Roux, *Bull. soc. chim.* [2] **46**, 273 (1886); *Compt. rend.* **102**, 1559 (1886).

tities of ethylene. No search was made for ketene. A small amount of toluene is also a product of the pyrolysis.

When heated at lower temperatures for longer periods of time, the course of the reaction [63] is decidedly different. Twenty percent of acetophenone may be recovered after 16 days of refluxing (200°), but in this process there is formed 20 percent of dypnone, C_6H_5—CO—CH=C(CH_3)—C_6H_5; 45 percent of 1,3,5-triphenylbenzene, and a slight quantity of α,β'-diphenyl-furan,  . Obviously, therefore, the major reaction in this case is the loss of three molecules of water from three of the ketone; and a lesser reaction is the loss of one molecule of water from two of the ketone. In both of these cases, the dehydration proceeds in a comparable manner.

As might be anticipated, somewhat different results are encountered when acetophenone is heated in a sealed tube. The isolation of 1.5 percent of sodium benzoate at 310° in 10 hours is rather novel, and 5.5 percent at 370° in 10 hours. The responsible factor for its production is the glass. At 310° and at 370°, the volumes of gaseous products are 300 cc. and 2500 cc. respectively. The analyses, by volume, are: carbon monoxide, 75 and 70 percent; carbon dioxide, 18 and 19 percent; methane, 6 and 10 percent; hydrogen, 1 and 1 percent. The non-gaseous products are indicated in the following table for temperatures between 290-370°; in each case, the duration of the experiment is 10 hours.

TABLE XXIX. *Non-Gaseous Products of the Pyrolysis of Acetophenone.*

Temperature Degrees Centigrade	Unrecovered Acetophenone Percent	Dypnone Percent	Triphenylbenzene Percent	Diphenylfuran Percent	Gases Cubic Centimeters
290	25	80	5	small	...
310	?	less	18	more	300
330	70	still less	37	10	?
350	?	" "	42	?	?
370	?	little	40	little	2500

The yields of the reaction products are based on the amount of unrecovered acetophenone. It seems that the optimum temperature for the production of dypnone is 290°; for diphenylfuran, 330°; and for triphenylbenzene, 350°. It was shown that α,β'-diphenylfuran may be synthesized from dypnone at 250° in the presence of nitrobenzene

[63] Engler and Dengler, *Ber.* **26**, 1445 (1893).

(oxidizing agent), but that none is formed in its absence: dypnone — 2H = diphenylfuran.

The decomposition temperature for *p*-methoxyacetophenone in a sealed tube is about 360°. Water, a little oil and a carbonized mass are the result of 20 hours of heating at 360-380°. *p*-Methoxypropiophenone is almost completely carbonized in 100 hours at the same temperature, as is the butyrophenone. Nevertheless, in all cases there is still a little unchanged ketone. In the latter case, and also with *p*-methoxy-*iso*butyrophenone, there is 80-86 percent recovery after 18 hours at 360°. It will be noticed that these ketones are considerably more stable than the corresponding hydrocarbons (p. 106). At the temperature at which these ketones are attacked, water has been shown to be a reaction product. The condensation products, which were undoubtedly formed, resinified and carbonized so rapidly that no simple products could be detected.

Dibenzyl ketone gives rise [64] to a considerable quantity of carbon monoxide, toluene, water and carbonaceous matter, by heating it in a tube for 14 hours at 200-360°. The pressure, which reached 12 atmospheres, was released at frequent intervals. Analysis of the gas showed that it was over three-fourths carbon monoxide. About a 50 percent yield of toluene was reported. Methane appeared at 390°. From the resinous residue, some unidentified crystals melting at 100° (from alcohol) were isolated. To explain these data, Engler assumed that hydrogen was liberated in the pyrolysis, and that it was the active agent in the formation of toluene and carbon monoxide:

$$(C_6H_5CH_2)_2CO + 2H \longrightarrow CO + 2C_6H_5CH_3.$$

Possibly the temperature of 200-360° is insufficient to induce an initial ketenic decomposition, but carbon monoxide, toluene and resinous matter are readily explained by such a mechanism:

$$C_6H_5CH_2—CO—CH_2C_6H_5 \longrightarrow [C_6H_5—CH=C=O] + C_6H_5—CH_3.$$

The phenyl ketene would probably decompose into carbon monoxide and polymerized phenylmethylene.

Stearone. Very little carbon monoxide is formed from stearone [65] at 300-350°. The quantity of carbon monoxide formed from stearone and oleone, respectively, by heating the former at 500-550° and the latter at 550-600°, is 48.10 percent and 66.96 percent of the theoretical. In addition to carbon monoxide, saturated and unsaturated hydrocarbons are formed, and small quantities of hydrogen and carbon dioxide.

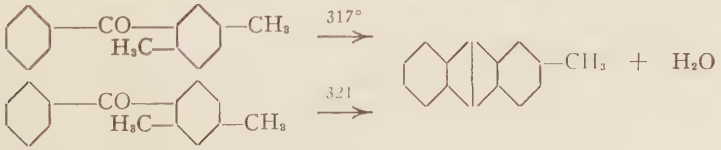
[64] Engler and Low, *Ber.* **26**, 1438 (1893).
[65] Sato and Ito, *J. Soc. Chem. Ind. (Japan)* **30**, 252 (1927); *Chem. Abstracts* **21**, 2372 (1927).

There is no evidence in the literature to indicate that ketones undergo pyrolysis into allenes. The possibility that acetone, $CH_3—CO—CH_3$, might change into allene, $CH_2=C=CH_2$, and water, has never been realized. One experiment [66] on a related subject deserves especial mention. A small amount of tetraphenyl allene is formed during the dry distillation of barium diphenylacetate. It was, therefore, assumed that symmetrical tetraphenyl acetone was an intermediate product, and that this changed into the allene with the loss of a molecule of water. This assumption has been recently disproved.[67] When this ketone, $(C_6H_5)_2CH—CO—CH(C_6H_5)_2$, is passed through a red-hot tube 10 cm. long, no tetraphenyl allene is formed. Although the products were not exhaustively studied, it was established that some crystalline symmetrical tetraphenyl ethane may be isolated from the oily mixture of products. It would be interesting to learn if diphenyl ketene is a product of this reaction.

The distillation of *β*-benzopinacolone [68] gives triphenylmethane, chiefly. Other products are *p*-benzoyl-triphenylmethane (a product of rearrangement), benzene, tetraphenyl-ethylene, and a compound $C_{19}H_{14}$, of melting point 144°, thought possibly to be phenyl fluorene. *β*-Benzopinacolone, $(C_6H_5)_3C—CO—C_6H_5$, may be regarded as a transition compound between aliphatic and aromatic ketones since the carbonyl group is attached to two tertiary carbon atoms.

Aromatic Ketones.

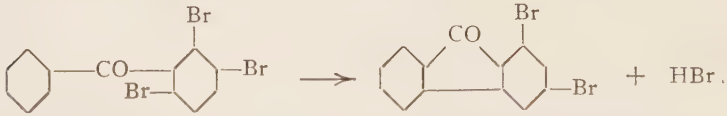
Benzophenone. At high temperatures, benzophenone [69] is largely unaffected by heat, but it does change in part into benzene and benzaldehyde. More elevated temperatures induce resinification. Benzophenone is stable when heated in a pressure apparatus at 430°, but it breaks down [56] completely at 500-550° largely into carbon and gases, but gives about 12 percent of a liquid containing benzene and diphenylmethane. If refluxed for several days, 2,4- or 2,5-dimethyl-benzophenone [70] gives 2-methyl anthracene. The yields are unstated.



[66] Vorländer and Siebert, *Ber.* **39**, 1024 (1906).
[67] Vorländer and Rack, *Ber.* **56**, 1125 (1923).
[68] Delacre, *Bull. soc. chim.* [4] **5**, 1144 (1909).
[69] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[70] Elbs and Larson, *Ber.* **17**, 2849 (1884); Elbs, *J. prakt. Chem.* [2] **35**, 472 (1887)

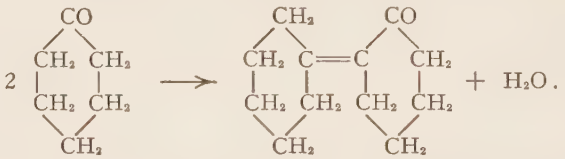
Di-*p*-xylyl ketone changes into trimethyl anthracene even by boiling with water.

When 2,4,6-tribromobenzophenone is heated [71] for several days at 400°, 1,3-dibromofluorenone is formed, admixed with some unchanged ketone:



Neither the dimethylamino group nor the hydroxy group occasion much instability in the benzophenone molecule, for Michler's ketone boils without decomposition at 360°, and *o,o'*-dihydroxy-benzophenone at 330-340°.

Cyclohexanone. This has been found [72] to undergo two different types of behavior towards heat, depending on the temperature. About five-sixths of it may be recovered after 115 hours of refluxing (153-156°), and the remainder is cyclohexylidene cyclohexanone:



This substance boils at 158-162° at 30 mm. and gives an oxime melting at 147-152°.

At 700°, cyclohexanone vapor decomposes quite rapidly into gaseous products. Twenty-eight grams of the ketone was found to yield 4710 cc. of gas. A sample of the gas taken near the beginning of the run was found to differ in percentage composition from a sample taken near the end; there is an increase in the percentage of carbon monoxide and of olefines with the progress of the reaction. The first and second values, respectively, are: carbon monoxide, 52 and 61 percent; olefine, 19 and 32 percent; hydrogen, 27 and 6 percent; saturated hydrocarbons, 2 and 0.1 percent. Both ethylene and propylene are present in the olefine mixture.

In the above experiment, the cyclohexanone was introduced into the hot furnace at a rate of about 5 drops a minute; the entire pyrolysis took somewhat over one hour. A negative search was made for ketene as a product of the reaction. About 4 grams of condensed liquid was formed, one-third of which is a mixture of water and cyclohexadiene-

[71] Montagne, *Rec. trav. chim.* **28**, 449 (1910).
[72] Hurd and Greengard, unpublished results.

1,3; and the remainder is unchanged cyclohexanone. This may be taken as evidence for the following equation:

$$C_6H_{10}O \longrightarrow H_2O + \begin{array}{l} CH{=}CH{-}CH \\ \quad\quad\quad\

Acetol acetate is both a ketone and an ester. From 42 grams of this substance, decomposed[76] during 5.5 hours at 430-450°, 18 grams is recoverable. The reaction products include 3 liters of gaseous products, and 6 cc. of low boiling material which is chiefly acetaldehyde. The latter, however, contains some crotonaldehyde and acetic acid.

Benzoin is also an α-hydroxyketone. It may be heated[77] for 2 days at 220-230° without change, but at 300° it undergoes complete pyrolysis in 2 hours. Fourteen grams of desoxybenzoin, $C_6H_5COCH_2C_6H_5$; 13 grams of benzil, $C_6H_5COCOC_6H_5$; and 3 grams of toluylene hydrate, $C_6H_5CHOHCH_2C_6H_5$ are the reaction products from 40 grams of benzoin, $C_6H_5COCHOHC_6H_5$. These data are convincing evidence that the major reaction is one of simultaneous oxidation and reduction. However, dissociation into smaller molecules is also evident, as witnessed by the isolation of 4 grams of benzaldehyde, 2 grams of benzoic acid (no diphenylacetic acid), and 1 gram of water. Similar results had also been obtained by Engler and Grimm,[78] who identified benzil, desoxybenzoin and diphenyl-methane as reaction products (10 hours at 280° in a sealed tube). They also established the presence of a small amount of benzaldehyde, and showed that the gaseous products of the reaction were 92 percent carbon dioxide and 8 percent carbon monoxide. Lachman's results were obtained in a sealed tube, but he demonstrated that similar results were obtainable by heating benzoin at 300-325° in a direct flame.

The gaseous decomposition[79] of benzoin may be catalyzed between 300-360° by mossy palladium or platinum. The gas consists chiefly of carbon monoxide and hydrogen. The other products of this reaction are benzene, benzil and benzophenone in varying amounts; there is also some benzoic acid and a trace of benzaldehyde.

β-Hydroxyketones. The β-hydroxyketones are similar to the aldols, but they appear to be more stable. Whereas aldol pyrolyzes below its boiling point (calculated to be 183°) into crotonaldehyde and water, methyl acetonyl carbinol, $CH_3COCH_2CHOHCH_3$, and diacetone alcohol, $CH_3COCH_2C(CH_3)_2$—OH, both boil[80] without decomposition (at 177° and 166° respectively). However, the former may be made to change into ethylidene acetone, $CH_3COCH{=}CHCH_3$, by heating at 250° in a sealed tube, or by long refluxing (2 or 3 days; the yield is 8 grams from 32 grams). The effect of catalysts[81] on this reaction is very

[76] Nef, *Ann.* **335**, 263 (1904).
[77] Lachman, *J. Am. Chem. Soc.* **46**, 708 (1924).
[78] Engler and Grimm. *Ber.* **30**, 2922 (1897).
[79] Knoevenagel and Tomasczewski, *Ber.* **36**, 2829 (1903).
[80] Claisen, *Ann.* **306**, 325 (1898).
[81] Kyriakides, *J. Am. Chem. Soc.* **36**, 534 (1914).

marked. Kyriakides recommends distillation with a trace of sulfuric acid, and other investigators [82] recommend distillation in the presence of a trace of iodine. The latter procedure works well with the conversion of diacetone alcohol to mesityl oxide, or heptanol-4-one-2 into butylidene acetone. However, it has been noticed [83] that hexanol-4-one-2, $C_2H_5CHOHCH_2COCH_3$, exerts a great tendency to lose a molecule of water by vacuum distillation. Usually, in such cases, there is not only the tendency for dehydration but also the tendency for scission into ketone and aldehyde, or with diacetone alcohol, into two molecules of acetone. Catalysts tend to offset this tendency of scission.

Derivatives of dimolecular diacetyl [84] are given a cyclic β-hydroxyketone structure. Thus, dimeric diacetyl may be

$$\begin{matrix} CH_3 & & CH_2{-}CO & & CH_3 \\ & >C< & & >C< & \\ HO & & CO{-}CH_2 & & OH \end{matrix}$$

from which some diacetyl is formed by vacuum distillation. A related compound, which is given the structure,

$$\begin{matrix} & & C_6H_5CH{=}C{-}CO{-}C(CH_3){-}OH \\ & & \quad | \qquad\quad | \\ HO{-}C{-}CO{-}CH{-}COC_6H_5 & & \\ \quad | & & \\ CH_3 & & \end{matrix}$$

decomposes at 250-270° in a vacuum, giving small yields of benzaldiacetyl, $C_6H_5CH{=}CH{-}CO{-}CO{-}CH_3$. This indicates a scission in the manner of simpler β-hydroxyketones. The other conceivable product of the scission, $CH_3COCOCH_2{-}COC_6H_5$, was not isolated.

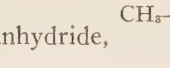
γ-Hydroxyketones. The structure [85] of pentanol-5-one-2 has not been definitely established; just as with the γ-hydroxyaldehydes, the structure may be lactonic. These two formulas are $CH_3{-}CO{-}CH_2CH_2CH_2OH$ and $\begin{matrix} CH_3{-}C(OH){-}CH_2{-}CH_2 \\ \quad | \qquad\qquad\quad | \\ O{-}\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-{-}CH_2 \end{matrix}$. At its boiling point, water is gradually eliminated, and there is produced a pleasant smelling anhydride, whose formula is either

$$\begin{matrix} CH_2{=}C{-}CH_2CH_2CH_2 \\ \quad | \qquad\quad | \\ \quad |{-}\!\!-O{-}\!\!-| \end{matrix} \quad \text{or} \quad \begin{matrix} CH_3{-}C{=}CHCH_2CH_2 \\ \quad | \qquad\quad | \\ \quad |{-}\!\!-O{-}\!\!-| \end{matrix},$$

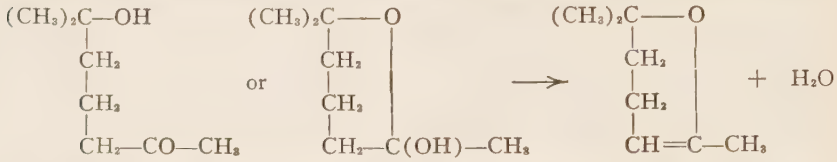
probably the latter

δ-Hydroxyketones. Hexanol-6-one-2 is a parallel case to the foregoing. Its structure may be considered either as open chain or

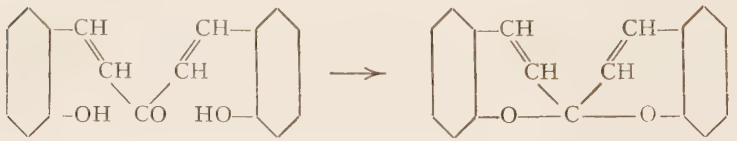
[82] Hibbert, *J. Am. Chem. Soc.* **37**, 1748 (1915); Grignard and Dubien, *Ann. chim.* [10] **2**, 288 (1924).
[83] Pastureau and Zamenhof, *Compt. rend.* **182**, 323 (1926).
[84] Diels, Blanchard and Heyden, *Ber.* **47**, 2357 (1914); Diels and others, *Ann.* **434**, 19 (1923)
[85] Perkin, Jr. and Freer, *Ber.* **19**, 2567 (1886).

cyclic; the anhydride,  , is formed by distillation[86] at ordinary pressure. The *gamma* and *delta* hydroxyketones bear a close relationship to carbohydrates.

Methyl-2-heptanol-2-one-6 loses a molecule of water[87] by distillation, even in a vacuum (boiling point (23 mm.) 124°, with decomposition). Instead of methyl heptenone, an isomeric cyclic oxide is produced. Thus:

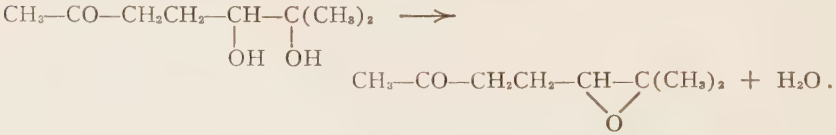


A somewhat similar dehydration, with ring closure, occurs[88] in the following case, above the melting point, 102°:



bis-(o-hydroxybenzal)-acetone *dibenzo*-spiro-*pyrane*

γ,δ-Dihydroxyketones. Hibbert and Burt[88a] have established that methyl heptenone oxide and water, the former in 60 percent yield, may be obtained by heating methyl γ,δ-dihydroxy*iso*hexyl ketone at 150° in a distilling flask. Since the oxide may be formed by the reaction of methyl heptenone and benzoyl hydroperoxide, this seems good evidence for the following reaction which is suggested:



On the other hand, it has been shown earlier that glycols do not undergo reactions of pyrolysis into ethylene oxide derivatives. Therefore some peculiar condition must be present in this case. In fact, methyl γ,δ-dihydroxypentyl ketone, the lower homolog behaves differently at 90° in the presence of a trace of sulfuric acid since it loses water between the carbonyl and the γ-hydroxyl. Heat alone at 150°, however, might give rise to different results.

[86] Lipp, *Ann.* **289**, 187 (1896).
[87] Verley, *Bull. soc. chim.* [3] **17**, 186 (1897).
[88] Decker and Felser, *Ber.* **41**, 2997 (1908).
[88a] Hibbert and Burt, *J. Am. Chem. Soc.* **50**, 1415 (1928).

THIOKETONES.

By a rapid distillation [89] of trithioacetophenone, there is obtained the blue, monomolecular, $C_6H_5CSCH_3$, in a rather pure state. It is partly decomposed by further distillation into styrene, ethyl benzene, diphenyl thiophene, and sulfur; after 4 or 6 distillations, the blue liquid becomes colorless. In explanation, the following equations were presented:

$$C_6H_5—CS—CH_3 \longrightarrow S + C_6H_5—CH=CH_2$$

and then,

$$2C_6H_5CH=CH_2 + 3S \longrightarrow H_2S + C_6H_5—C_4H_2S—C_6H_5$$
$$C_6H_5CH=CH_2 + H_2S \longrightarrow S + C_6H_5—CH_2CH_3.$$

Thiobenzophenone is largely charred [90] on distillation with the formation of hydrogen sulfide and tetraphenyl ethylene. Very probably, sulfur is eliminated, and this reacts at the high temperature to produce carbon and hydrogen sulfide. If the distillation is performed in the presence of copper,[91] tetraphenylethylene is formed quantitatively:

$$2(C_6H_5)_2CS \longrightarrow (C_6H_5)_2C=C(C_6H_5)_2 + 2S.$$

It will be recalled that this compound was also formed (p. 137) by the action of heat on diphenylbromomethane, and on benzophenone bromide.

DIKETONES.

α-Diketones. Diacetyl is the only simple α-diketone, the pyrolysis of which has been studied. When the vapors of this substance [92] are passed through an electrically heated glass tube, filled with pieces of glazed porcelain, ketene is produced between temperatures of 605-675°; the maximum yield of 14.5 percent comes at 615°. This is considerably below the temperature (700°) found to be best for ketene production from acetone. These results are tabulated below.

TABLE XXX. *Pyrolysis of Diacetyl.*

Temperature °C.	Time, Minutes	Amount Used	Amount Condensed	Amount Decomposed	Yield of Ketene, Percent
		Cubic Centimeters			
605	60	40	9	31	10.8
615	146	73.5	20	53.5	14.5
625	74	45	13	32	13.9
675	78	35	2	33	3.3

[89] Baumann and Fromm, *Ber.* **28**, 895 (1895).
[90] Behr, *Ber.* **5**, 970 (1872).
[91] Gattermann, *Ber.* **29**, 2945 (1896).
[92] Hurd and Tallyn, *J. Am. Chem. Soc.* **47**, 1781 (1925).

The gaseous products of the reaction were not investigated, but it is reasonable to assume that carbon monoxide was liberated. Then:

$$CH_3—CO—CO—CH_3 \longrightarrow CH_2=C=O + CO + CH_4.$$

Phenanthraquinone is an α-diketone that distils with no decomposition above 360°. However, it changes into diphenylene ketone [93] if it is distilled over burnt lime. Small quantities of fluorene are also formed. Lead oxide may also be used, in which case [94] the carbon monoxide becomes oxidized to carbon dioxide, but soda lime gives an almost quantitative yield of diphenyl.

β-Diketones. *Acetylacetone* is the simplest β-diketone. At ordinary temperatures it is known to exist [95] in the enolic modification to the extent of 76-83 percent; $CH_3—CO—CH=C(OH)—CH_3$. This equilibrium value with its keto isomer probably changes very decidedly towards the keto as the temperature rises. From a standpoint of pyrolysis, therefore, the diketo formula will be employed.

Acetylacetone is unusually interesting since there are three possible ways by which decompositions to ketenes might occur, accompanied in each case by methane:

$$CH_3COCH_2COCH_3 \longrightarrow CH_2=CO + CH_4 + OC=CH_2$$

or

$$\longrightarrow CH_3CO—CH=C=O + CH_4$$

or

$$\longrightarrow CH_4 + OC=C=CO + CH_4.$$

Ketene, acetyl ketene (or cyclobutanedione-1,3), and carbon suboxide are possible residues. Of these three, ketene alone is found in practice.[96] Carbon suboxide cannot have even a transient existence, since it is prepared in good yields (see p. 535) by other pyrogenic methods.[97] If the first equation is correct, it is the central carbon atom of acetylacetone which is expelled as methane.

Although the condensate in this reaction is largely unchanged acetylacetone, it contains in addition small amounts of lower- and of higher-boiling material. Presumably the lower-boiling liquid is acetone. This would lend some weight for a consideration of the equation:

$$CH_3COCH_2COCH_3 \longrightarrow CH_3COCH_3 + CH_2=C=O.$$

There are two objections to it, however. First, the quantity of low-boiling material (acetone) in the condensate is slight. Second, at 700°, the yield of ketene from acetylacetone diminishes to a small value.

[93] Anschütz and Schultz, *Ber.* **9**, 1402 (1876); *Ann.* **196**, 44 (1879).
[94] Wittenberg and Meyer, *Ber.* **16**, 502 (1883).
[95] Hieben, *Ber.* **54**, 902 (1921); Meyer and Hopff, *ibid.*, p. 579.
[96] Hurd and Tallyn, *J. Am. Chem. Soc.* **47**, 1779 (1925).
[97] Ott and Schmidt, *Ber.* **55**, 2126 (1922).

Since this is the optimum temperature for the production of ketene from acetone, it is illogical to assume that acetone is a major product of the reaction. The following table gives the data for the decompositions.

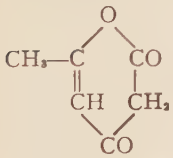
TABLE XXXI. *Pyrolysis of Acetylacetone.*

Temperature °C.	Time, Minutes	Ketone Used	Amount Condensed	Ketone Decomposed	Yield of Ketene, Percent
		——Cubic Centimeters——			
585	16	35	27	8	3.7
610	20	52	47	5	14.1
635	15	35	29	6	16.7
650	18	32	19	13	10.8
675	23	43	26	17	9.6
700	9	31	21	10	4.8

It is of more than passing interest to learn that diacetyl and acetylacetone behave so similarly towards heat. Both give ketene in about the same yield at about the same temperature.

Benzoylacetone. When benzoylacetone is heated [98] at 300° for 10 hours, no gaseous products arise, but some high boiling condensation products are formed which react with the water that is produced to give either benzoic acid and acetone, or acetic acid and acetophenone.

Triacetic acid lactone is considered to have the structure,

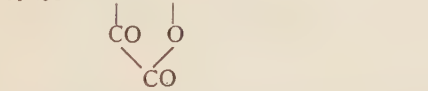


or its enol. At 250°, it breaks down [99] with the production of acetylacetone and carbon dioxide.

A reaction resembling disproportionation occurs when dibenzoylphenyl-methane [100] is heated in a limited volume of alcohol. The material gradually goes into solution, and tribenzoyl-phenyl-methane precipitates on cooling:

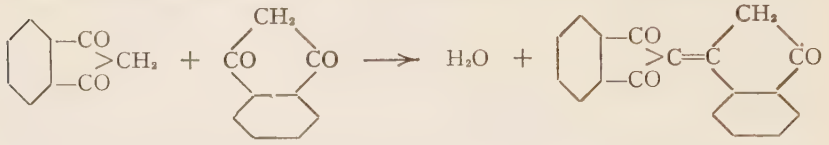
$$2C_6H_5CH(COC_6H_5)_2 \longrightarrow C_6H_5C(COC_6H_5)_3 + C_6H_5CH_2{-}COC_6H_5.$$

"Ketophenylparacophenone" is not only a β-diketone, but also an α-ketonic lactone. By long heating [101] at 220-230°, carbon monoxide and carbon dioxide are eliminated in equal volumes, and benzalacetophenone comprises the residue:

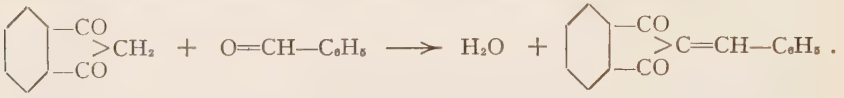


[98] Engler and Grimm, *Ber.* **30**, 2924 (1897).
[99] Collie, *J. Chem. Soc.* **59**, 607 (1891).
[100] Meisenheimer and Weibezahn, *Ber.* **54**, 3195 (1921).
[101] Knoevenagel and Schmidt, *Ann.* **281**, 48 (1894).

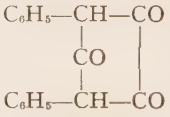
1,3-Diketohydrindene is dehydrated[102] at 120-125° to anhydrobisdiketohydrindene. The conversion may be made nearly quantitative if the compound is heated several hours at 100° with 5 parts of water.



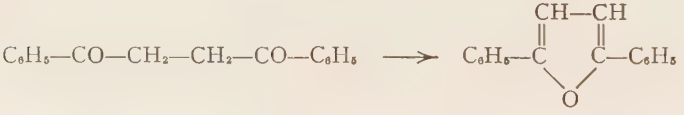
This decomposition is exactly analogous to the reaction of diketohydrindene and benzaldehyde, which also takes place at 120°:



When the diketohydrindene is maintained for 12-24 hours at 120-125°, it becomes further dehydrated[103] to truxene-quinone. This may be separated from the other compound, which is also present, by its insolubility in alkali.

1,3-Diphenyl-2,4,5-triketopentamethylene,  , melts[104] at 192°, then resolidifies; at 240° it melts again as an isomer.

Other Diketones. Symmetrical dibenzoylethane becomes transformed[105] into an 80 percent yield of α,α'-diphenyl-furan by heating 18 hours at 300-310° in a sealed tube:



A study of other diketones of this type: Ar—CO—$(CH_2)_{2\text{ to }5}$—CO—Ar, shows that, as with paraffin chains, those with an even number of carbon atoms are distinctly more reactive than those with an odd number. Thus, *dibenzoyl-propane,* a 1,5-diketone, after 20 hours at 320-330°, permits of 20 percent recovery; the reaction products include acetophenone, and an oil which was thought to be composed of condensation products of acetophenone and vinyl phenyl ketone. *Dibenzoyl-butane,* a 1,6-diketone, gives rise to an ill-defined polymerization product in 2 hours at 340°.

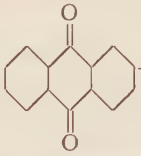
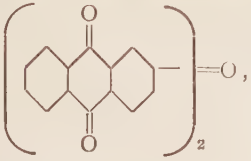
[102] Wislicenus and Kötzle, *Ann.* **252**, 77 (1889).
[103] Kostanecki and Laczkowski, *Ber.* **30**, 2143 (1897).
[104] Claisen and Ewan, Ber. **27**, 1353 (1894); *Ann.* **284**, 250 (1895).
[105] Skraup and Guggenheimer, *Ber.* **58**, 2488 (1925).

Replacement of the phenyl in these compounds by *p*-chlorophenyl results in an increased sensitiveness to temperature and in fewer secondary reactions. For example, di-*p*-chlorobenzoylpropane, $(CH_2)_3<^{CO—C_6H_4Cl}_{CO—C_6H_4Cl}$, is almost unchanged after 4 hours at 302°, whereas the corresponding butane derivative is decidedly altered in 24 hours at 260°. From 5 grams of the latter, there was found 2 grams of chlorophenyl-chlorobenzoyl-cyclopentene (2 isomers) and 1 gram of polymerization products. At 320° and 50 hours, polymerization products, carbonization, and the formation of *p*-chlorobenzoic acid were reported.

Di-*p*-chlorobenzoylpentane, a 1,7-diketone, decomposes in 13 hours at 285-295° into a dark, viscid oil. A very small amount of yellow needles, $C_{19}H_{16}OCl_2$, and a little *p*-chlorobenzoic acid were isolated from this mixture.

Quinones.

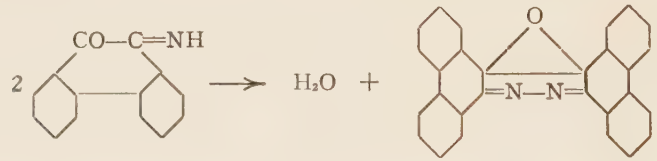
Quinones have not been studied very thoroughly for their behavior towards heat. Benzoquinone [106] is stated to yield a mixture of hydroquinone, quinhydrone, etc., when it is heated in a tube at 160°.

Anthraquinone begins to pyrolyze [107] at 450°. Two molecules appear to condense with the elimination of two oxygen atoms. Sodium anthraquinone-2-sulfonate,  , gives 35 percent of its weight of distillate [108] when it is destructively distilled in a combustion furnace from a copper tube. From 150 grams of this distillate, the investigators were able to isolate 55 grams of anthraquinone and 7 grams of 2-hydroxyanthraquinone by extracting with acetic acid. By 6 xylene extractions of the residue, 57 grams (melting point 266-280°) dissolved in the first three fractions and 11 grams in the last three. From the latter, 8.7 grams of pure 2,2′-dianthraquinonyl ether  ,

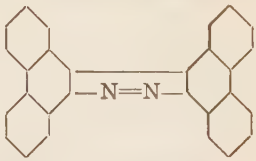
[106] Scheid, *Ann.* **218**, 227 (1883).
[107] Lewis and Shaffer, *Ind. Eng. Chem.* **16**, 717 (1924).
[108] Perkin and Perkin, *J. Chem. Soc.* **47**, 679 (1885); Perkin and Sewell, *ibid.* **123**, 3032 (1923).

was isolated, and from the first xylene fraction small quantities of 2,2′-dianthraquinonyl sulfide.

Phenanthraquinone has already been discussed (p. 264). Phenanthraquinone imide becomes dehydrated to its anhydride [109] in 30 percent yield when the imide is heated to 250° ; better yields are obtained if the imide is boiled for 15 minutes in acetic anhydride.

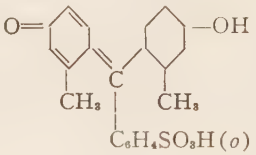


The latter compound melts at 252°. If it is heated to faint redness in a platinum crucible, the atom of oxygen is lost, and



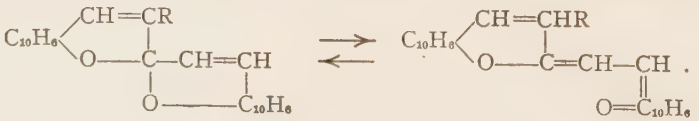
is formed in 70 percent yields.

The colorless, lactoid form of the dimethyl ether of thymol-sulfonephthalein rearranges [110] at 180° into the colored, quinoid form. Similarly, the dimethyl ether of *m*-cresol-sulfonephthalein,



also exists [111] in two forms, the colorless and the red. The latter, which has the quinoid structure, is produced from the former by 20 minutes' heating at 170-172° in an atmosphere of carbon dioxide.

The *spiro*-dinaphthopyrans [112] are of interest because their colorless solutions in hydrocarbon solvents begin to turn blue-violet at 80-100°, and the color becomes deeper if the temperature is increased. This behavior may be explained on the basis of the reversible equation:



[109] Schönberg and Rosenthal, *Ber.* **54**, 1789 (1921).
[110] Orndorff and Cornwall, *J. Am. Chem. Soc.* **48**, 990 (1926).
[111] Orndorff and Purdy, *ibid.*, p. 2218.
[112] Löwenbein and Katz, *Ber.* **59**, 1377 (1926).

An interesting pyrolysis that is related to ketones [113] is the following:

$$(C_6H_5)_2C(NH_2)—ONa \longrightarrow C_6H_6 + C_6H_5—CO—NHNa.$$

The original compound is synthesized by the addition of sodamide to benzophenone in benzene or toluene. It has already been mentioned on p. 34 that this method may be used in the determination of the affinity capacity of various radicals. Thus, *p*-dimethylaminobenzophenone reacts in both possible ways, giving $C_6H_6 + (CH_3)_2N—C_6H_4—CONHNa$, and $C_6H_5—N(CH_3)_2 + C_6H_5—CO—NHNa$. This method serves only with tertiary ketones, since a compound such as methylethyl ketone would give a salt with sodamide. *p*-Dimethylaminophenyl and *p*-anisyl are thus found to be more firmly attached to carbon in these cases than phenyl, but the chlorophenyl and the bromophenyl radicals are less so. The triphenylmethyl radical is still less firmly attached, as shown by the work with the ketone, $(C_6H_5)_3C—CO—C_6H_5$.

[113] Schönberg and others, *Ann.* **436**, 205 (1924).

CHAPTER 11.

CARBOHYDRATES, WOOD AND COAL.

The presence of hydroxyl and carbonyl groups in carbohydrates makes this a fitting place to discuss their behavior towards heat. Wood and coal are obviously mixtures, and as such are not included in the scope of the monograph. However, they are related to carbohydrates and it will be interesting to discuss their modes of thermal decomposition from this viewpoint.

Carbohydrates.

Monosaccharides.

Glucose. In 1860 Gélis discovered that glucose [1] is converted into glucosan at 170°, some 25° above the melting point. Recently, this reaction:

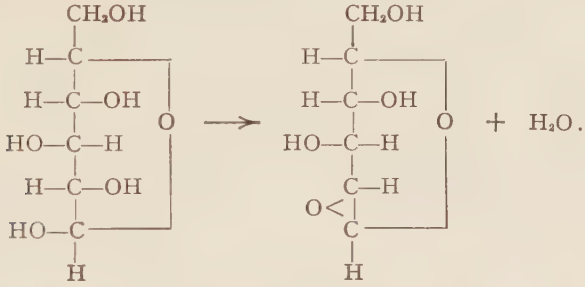
$$C_6H_{12}O_6 \longrightarrow H_2O + C_6H_{10}O_5,$$

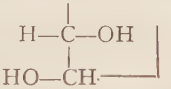
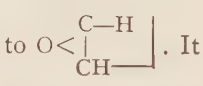
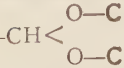
has been shown to give a 92 percent yield of pure glucosan, by performing the dehydration [2] at 150-155° in a vacuum of 15 mm. Caramel is formed [3] when glucose, or sucrose, is heated at 230° with a little water. No doubt the change is very similar. In a very recent article, Pictet and Vogel recommend a temperature of 145°, a pressure of 15 mm. and a duration of 2 hours as the conditions [4] for the conversion of glucose into glucosan. They also find that by heating equimolecular mixtures of α- and β-glucose in a vacuum at 160°, the mixture melts and then suddenly resolidifies, the temperature remaining at 160°. Maltose, $C_{12}H_{22}O_{11}.H_2O$, is the product of this reaction. A patent dealing with the production of "tetraglucosan" from grape sugar [5] recommends heating under diminished pressure, or in an inert gas, in the presence of a small quantity of ferrous or manganous sulfates, with or without such diluents as vaseline oil or phenanthrene.

Glucosan is considered to possess an ethylene oxide ring, in addition to the butylene or amylene oxide ring which was originally present in

[1] Gélis, *Compt. rend.* **51**, 331 (1860); *J.* **1860**, 510.
[2] Pictet and Gastan, *Helv. Chim. Acta* **3**, 645 (1920); *Compt. rend.* **171**, 243 (1920).
[3] Beal and Bowey, *J. Am. Pharm. Assoc.* **12**, 495 (1923); Beal and Applegate, *ibid.*, p. 850.
[4] Pictet and Vogel, *Helv. Chim. Acta* **9**, 806 (1926); *Compt. rend.* **184**, 1512 (1927).
[5] Kerb, Brit. 243,348, Nov. 20, 1924, *Chem. Abstracts* **20**, 3697 (1926).

the glucose molecule. The best evidence at present [6] seems to favor the amylene oxide configuration, but as Irvine [7] points out, "it is perhaps necessary to emphasize that only in the cases of tetramethyl glucose and of tetramethyl galactose are we justified in allocating a fixed position to the internal oxygen ring". Certainly, one should realize that far different conditions of structure are apt to prevail at the melting temperature from the ones at room temperature. In assigning the amylene oxide formula, therefore, it should be kept in mind that this is not the exclusive formula for the representation of glucose. The equation to represent the production of glucosan is as follows:

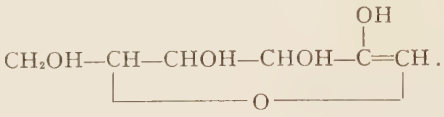


In some respects, the formulas of glucose and glucosan may be considered to bear a resemblance to those of glycol and ethylene oxide, since there is an apparent change from  to  . It was pointed out on p. 177 that compounds with the glycol configuration do not become dehydrated by thermal means to compounds of the ethylene oxide type. A close inspection of the formula of glucose reveals that its glycollic hydroxyl groups are not the ones which participate in this change. Of the two hydroxyls that do participate, one is part of a hemi-acetal configuration. Thus, the essential part of the molecule is not R—CHOH—CHOH—R, but R—CHOH—CHOH—OR′, wherein the R′ represents one of the carbon atoms in the R chain. The simple hemi-acetals (p. 244) break down into acetals as one of the products of decomposition. It is, therefore, interesting to note that the formula assigned to glucosan is an "acetal", since it contains the grouping  .

One detail of the above process deserves mention. The glucose formula contains a hydrogen on the carbon atom α to the hemi-acetal

[6] Charlton, Haworth and Peat, *J. Chem. Soc.* 1926, 89.
[7] Irvine, *Chem. Reviews* 4, 213 (1927).

hydroxyl, but there appears to be no dehydration to form the unsaturated compound,



Gamma- or *delta*-hydroxyaldehydes (p. 243), with an analogous structure, eliminate water by distillation under reduced pressure to form an unsaturated compound. Of course, in the known cases of this type which have been considered, only one available hydroxyl group has been present. Therefore, it is not yet known, except with carbohydrates, whether or not a compound of the ethylene oxide type could be formed by the pyrolysis of an α,γ- or an α,δ-dihydroxy-caproic aldehyde.

Fructose. Fructose melts between 95-105°. It changes into levulosan [8] by heating under diminished pressure to 140-160°. Recent directions by Pictet and Reilly [9] describe the preparation of levulosan from levulose, in unstated yields, by heating for 2-3 hours at 115-120° and 15 mm. pressure.

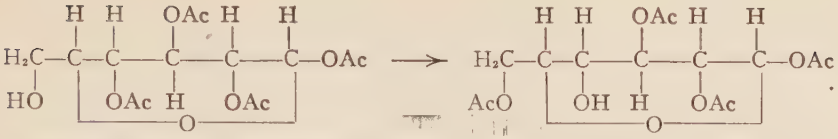
As will be subsequently shown, levulosan and glucose are the products formed if crude sugar is heated momentarily at 160°.

Galactose. When submitted to the progressive action of heat, this hexose [10] undergoes both dehydration and polymerization, but the two reactions occur at such neighboring temperatures that it is difficult to isolate the anhydride, galactosan, free from isomers. Galactosan is formed at a temperature of 135° and a pressure of 2 mm., but even with these conditions it is considerably contaminated with polymers.

Other Substances Related to Monosaccharides. Small yields of mannitan, $C_6H_8O(OH)_4$, come by heating *d*-mannitol [11] to 200°. When heated in a vacuum, mannitol [12] yields some *iso*mannide, $C_6H_{10}O_4$. Long heating of dulcitol [13] at 200° gives dulcitan, $C_6H_8O(OH)_4$. Undoubtedly, the dehydration in these reactions involves two hydroxyl groups and the formation of a 5- or a 6-membered ring.

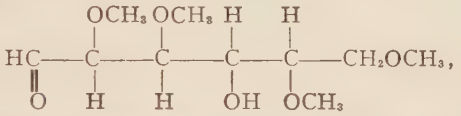
If 1,2,3,4-β-tetraacetyl-*d*-glucose [14] is heated for 3 hours at 140° in an ordinary glass apparatus there is an acetyl wandering, as indicated in the following equation:

[8] Hönig and Schubert, *Monatsh.* **8**, 545 (1887).
[9] Pictet and Reilly, *Helv. Chim. Acta* **4**, 613 (1921).
[10] Pictet and Vernet, *Helv. Chim. Acta* **5**, 444 (1922).
[11] Berthelot, *Ann. chim.* [3] **47**, 302 (1856).
[12] Fauconnier *Compt. rend.* **95**, 991 (1882); *Bull. soc. chim.* [2] **41**, 119 (1884).
[13] Berthelot, "Chimie organique fondée sur la synthèse," II, Paris, 1860, p. 209.
[14] Helferich and Kleni, *Ann.* **455**, 173 (1927).



Curiously enough, this change does not occur in quartz or in Jena glass, but platinum apparatus may be used.

In small amounts, tetramethyl mannose[15] may be distilled in a vacuum without appreciable pyrolytic changes. However, when 258 grams of this substance,

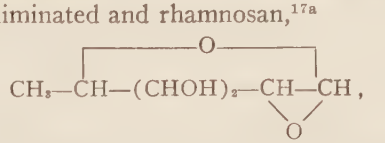


is heated in a 500 cc. Claisen flask at 130-170° and 5-30 mm., there is a distillate and a carbonaceous residue of about 50 grams. Refractionation of the distillate gives somewhat less than 10 percent of tetramethyl glucose, and three other fractions the identity of which is still in doubt. Probably they are mixtures. One fraction boiled at 108-115° and 1 mm.; it contained 47.78 percent methoxyl, and possessed a specific rotation of + 32.6°; another fraction, boiling point (4 mm.) 62-67°, was optically inactive, acidic, and possessed a methoxyl content of 44.44 percent; the third fraction, boiling point (5 mm.) 67-90°, was also optically neutral, less acidic than the former, and was 38.68 percent methoxyl.

It has already been mentioned[16] that glycollic aldehyde (p. 242), arabinose, sucrose, starch and cellulose yield products by dry distillation, which, after steam distillation, give a scarlet colored nickel derivative, indicating diacetyl.

The identity of furfural[17] as a product of pyrolysis of xylose has recently been established in the author's laboratory. The yield is small, however (1.3 percent); the conditions are as follows: a 4-gram sample is heated for 3.5 hours in a 25 cc. distilling flask at 100 mm. and 158° (bath temperature). Furfural appears in the distillate; the residue has a light caramel color. Possibly the residue is an anhydro-xylose.

If rhamnose is maintained for four hours at 150-155° and 15 mm. pressure, water is eliminated and rhamnosan,[17a]



[15] Greene, Dissertation, Northwestern University, 1927; Greene with Lewis, J. Am. Chem. Soc. 50, 2817 (1928).
[16] Schmalfuss and Barthmeyer, *Ber.* 60, 1035 (1927).
[17] Hurd and Isenhour, unpublished results.
[17a] Vogel, *Helv. Chim. Acta*, 11, 442 (1928).

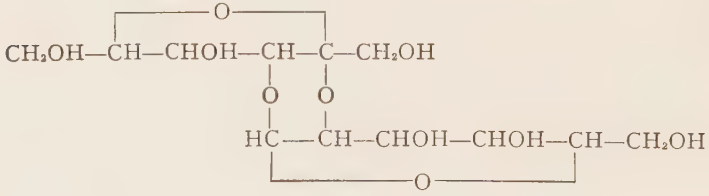
remains as the residue. Rhamnosan regenerates rhamnose by boiling with water.

If either *l*-arabonic lactone, or *l*-ribonic lactone, is heated [18] there results a pyrolysis giving 35 percent of a mixture of furoic and *iso*-pyromucic acids.

Disaccharides.

Lactose, maltose and sucrose all form anhydrides when they are heated in a vacuum at a moderate temperature. Lactose changes into lactosan, $C_{12}H_{20}O_{10}$, by maintaining [19] it for 10-12 hours at 185° and 4-6 mm. Its properties indicate that it is ε-galactosylgalactosan. The water of crystallization may be expelled from maltose [20] by heating at 145° at atmospheric pressure. By continuing the heating at 160° and 15 mm., a molecule of water may be eliminated, thereby leaving a residue of maltosan, $C_{12}H_{20}O_{10}$.

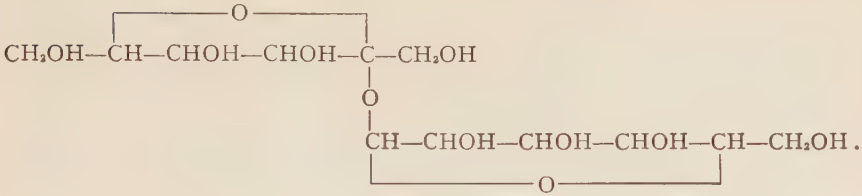
Sucrose (melting point 183°) successively loses water from 1, 2, and 3 molecules of the sugar when it is heated [21] at 185-190° and 15 mm. The loss in weight, respectively, is 5, 10, and 15 percent of the weight of the original sugar. In turn, there are formed *iso*saccharosan $C_{12}H_{20}O_{10}$, caramelan $C_{24}H_{36}O_{18}$, and caramelene $C_{36}H_{50}O_{25}$. The structure given by Pictet for *iso*saccharosan, modified to represent the glucose residue with an amylene oxide ring, is:



Isosaccharosan

The structure for sucrose is given below in comparison. Although the question regarding the structure of sucrose [22] is still an open one in some details, the following is the one which can be most strongly supported at the present time:

[18] Hasenfratz, *Compt. rend.* 184, 210 (1927).
[19] Pictet and Egan, *Helv. Chim. Acta* 7, 295 (1924).
[20] Pictet and Marfort, *ibid.* 6, 129 (1923).
[21] Pictet and Andrianoff, *ibid.* 7, 703 (1924).
[22] Irvine, *Chem. Reviews* 4, 220 (1927).



Sucrose

In the absence of evidence to the contrary, it would seem that the best interpretation of the reaction mechanism is to assume that the *iso*saccharosan was formed as the result of the interaction of glucosan and levulosan. Many years ago, Gélis found [23] that if sucrose is maintained for a few seconds above its melting point, there is no loss in weight but that glucose and levulosan are formed:

$$C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6 + C_6H_{10}O_5.$$

In Pictet's experiments, this reaction also occurred; further heating produced glucosan from glucose, and then the glucosan and levulosan were free to interact with each other. In confirmation of this mechanism, it was found that *iso*saccharosan is formed when a mixture of glucosan and levulosan are heated at 185° under a pressure of 15 mm., and also when a mixture of glucose and levulosan are similarly heated until there is a loss in weight of 5 percent. Pictet [24] has patented the method of preparation of such anhydro-sugars, or their polymers, by heating such disaccharides as sucrose or lactose at 185° or higher under diminished pressure.

Reilly [25] has conducted some interesting experiments on the dry distillation of sucrose at 10-15 mm. In the experiments which have been mentioned, no distillate was collected but the purpose was to obtain the anhydro-sugars in the residue. In Reilly's experiment, there was obtained 20.6 percent of a gas, 37.2 percent of an aqueous fraction which was condensed by a freezing mixture, after having first removed 11.6-15.3 percent of a viscid distillate at 60°. The residue of carbon in the flask weighed 30.6 percent of the total, and was rendered porous by the escaping gases. An empirical formula for the viscid distillate was $C_{12}H_{18}O_9$. It was pointed out that this sirup was different from levoglucosan or levo-levulosan, and it seemed to be a mixture of hexose anhydrides.

The aqueous fraction contained acetone, acetic acid and furfural, whereas the gases contained formaldehyde, carbon dioxide, carbon mon-

[23] Gélis, *Ann. chim.* [3] **52**, 352 (1858); **57**, 234 (1859).
[24] Pictet, U. S. 1,602,549, Oct. 12, 1926; *Chem. Abstracts* **20**, 3696 (1926).
[25] Reilly, *J. Soc. Chem. Ind.* **40**, 249T (1921).

oxide and hydrocarbons. In a separate distillation, conducted at 1-5 mm., carbon dioxide predominated in the first portion of gas, carbon monoxide in the second, and methane (and homologs) in the last. Unsaturated hydrocarbons were present throughout.

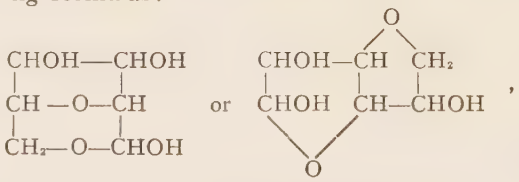
Inulin changes into trifructosan (9 grams from 10) by 3 hours' heating in glycerol at 120° and 15 mm. pressure.[25a] If it is heated for 6 hours at 140°, difructosan results.

STARCH.

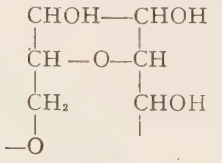
One of the first effects of heat on starch is a conversion into dextrin, a process which is undoubtedly started by the flatiron whenever starched goods are ironed. The fact that dextrins are more readily water soluble than starches becomes, therefore, a point of more than passing interest insofar as laundries are concerned. Dextrin may be prepared in quantity by heating starch for about 10 minutes at 180-200°. After it has cooled, the dextrin which has formed is readily separated from the unchanged starch by dissolving it in water.

Perhaps the most important product formed by the dry distillation [26] of starch is levo-glucosan; low pressures are used. Pringsheim [27] has recently indicated a 50 percent yield of *levo*-glucosan by dry distillation in a vacuum. *Levo*-glucosan is also formed when dextrin or cellulose is treated similarly.

Concerning the structure of *levo*-glucosan, Pictet suggests either of the two following formulas:

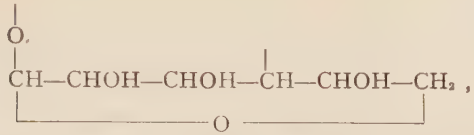


and considers that the nucleus of starch or cellulose is

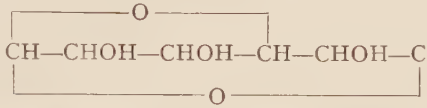


Pringsheim suggests a different explanation. According to him, the glucose radical in starch is assumed to be

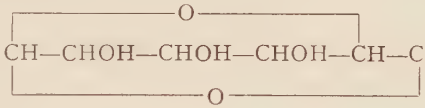
[25a] Pictet and Vogel, *Helv. Chim. Acta*, **11**, 215 (1928).
[26] Pictet and Sarasin, *Helv. Chim. Acta* **1**, 78 (1918); Pictet and Gaudet, *ibid.* **2**, 698 (1919); Pictet and Cramer, *ibid.* **3**, 640 (1920).
[27] Pringsheim and Steingroever, *Ber.* **57**, 1579 (1924).



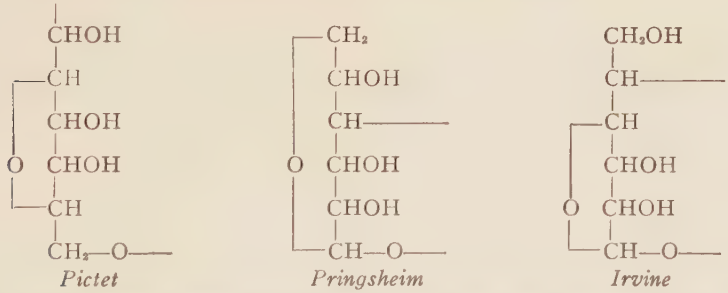
and that the formula for *levo*-glucosan differs from this only by a ring-closure at the unattached bonds:



Haworth's suggestion [28] regarding the formula of *levo*-glucosan is similar to Pringsheim's, but differs in having an amylene-oxide ring in place of the butylene-oxide ring; thus,



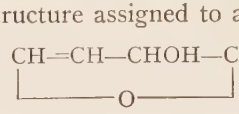
Neither Pictet's formula for the glucose residue in starch, nor Pringsheim's, is in agreement with Irvine's most recent suggestion.[29] All three types are presented below in parallel fashion to bring out the points of similarity and dissimilarity.



The following facts are known regarding *levo*-glucosan. It has no free carbonyl group; it has three hydroxyls; and it is very stable to heat. A small amount of *levo*-glucosan appears [30] as a sublimation product when starch is heated at ordinary pressure at 190-220°. It is also produced in the vacuum distillation of such glucosides [31] as salicin, arbutin and phlorhizin. In turn, saliretin, hydroquinol, phloretic acid and some phloroglucinol are also generated. Digitoxin, a glucoside

[28] Haworth, *J. Soc. Chem. Ind.* **46**, 300T (1927).
[29] Irvine, *Chem. Reviews* **4**, 226 (1927).
[30] Karrer and Rosenberg, *Helv. Chim. Acta* **5**, 575 (1922).
[31] Pictet and Gaudet, *loc. cit.*, ref. 26.

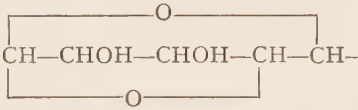
with the formula $C_{42}H_{66}O_{13}.\frac{1}{2}H_2O$, gives a sublimate of an anhydrodigitoxose,[32] $C_6H_{10}O_3$, by distilling in a vacuum of 0.03 mm. and 260-270°. The structure assigned to anhydrodigitoxose [33] is:



This is in contrast to Cloetta's [34] results, who obtained a sublimate of $C_8H_{14}O_4$, by heating digitoxin, $C_{44}H_{70}O_{14}$, in a vacuum.

A trihexosan, $(C_6H_{10}O_5)_3$, which is not triamylose, may be formed when potato starch [35] is kept in ten parts of glycerol for 45 minutes at 200-210°; if the experiment is stopped when the red color test with iodine is the brightest, a hexahexosan is formed. Pictet [36] believes that trihexosan is the ultimate product of the action of heat on starch. Since it may be hydrolyzed to dextrose and dihexosan, trihexosan appears to be β-glucosyldihexosan.

By heating lichenin [37] at 240° in glycerol, it is broken down in 30 percent yield to lichosan. If the latter is left in water solution, it repolymerizes to the original, identical lichenin in a few days. The formula ascribed by Pringsheim for lichosan is:



It is interesting to note that lichenin acetate [38] gives a 60 percent yield of lichosan acetate by heating at 235° in naphthalene. The lichosan prepared by the hydrolysis of the acetate is the same as that prepared by heating lichenin in glycerol.

Cellulose.

Cotton loses 6 to 8 percent of its weight at 100°, but regains it in moist air Structural decomposition [39] sets in at 162°. Its textile properties are destroyed at 249°, at which temperature a brown coloration appears. When cellulose [40] is heated at 190-250°, it yields a product, the aqueous extract of which gives an osazone, melting point 202°.

[32] Windaus and Freese, *Ber.* **58**, 2503 (1925).
[33] Windaus and Schwarte, *Nachr. Ges. Wiss. Göttingen Math. Physik. Klasse*, **1926**, 1; *Chem. Abstracts* **21**, 3618 (1927).
[34] Cloetta, *Arch. exp. Path. Pharmakol.* **88**, 113 (1920); *Chem. Abstracts* **15**, 707 (1921).
[35] Pictet and Jahn, *Helv. Chim. Acta*, **5**, 640 (1922); Pictet and Stricker, *ibid.* **7**, 932 (1924).
[36] Pictet and Salzman, *Helv. Chim. Acta* **7**, 934 (1924).
[37] Pringsheim, Knoll and Kasten, *Ber.* **58**, 2135 (1925).
[38] Pringsheim and Routala, *Ann.* **450**, 255 (1926).
[39] Matthews, *Color Trade J.* **12**, 255 (1923).
[40] Bain and Kay, *Trans. Roy. Soc. Can.* **18**, Sect. III, 269 (1924); Bain and Chute, *ibid.* **20**, Sect. III. 189 (1926).

Absorbent cotton, which had been previously extracted for 7 days with boiling water, if heated for 3 hours in an electric oven at 200° becomes brown-colored, and becomes partially water soluble. The average amount of sirup which was extracted by boiling water (after the 200° heating) is 3.36 percent. In this sirup, glucose, but no other hexose, is present. Its quantity appears to be between 7.5 and 13.6 percent of the sirup. The sirup contains some formic acid, and possibly some acetic acid, but no pentoses or methyl pentoses. At 200°, cotton [41] gives off almost no volatile products of pyrolysis, and the substances formed can only be discovered by extraction with a solvent. Cellulose appears to decompose slowly at 210-265°, with the ultimate formation of a rather stable, brown, brittle residue.

A gradual decomposition of cellulose occurs when it is heated under pressure [42] in benzene at 250-260°. No gas is formed, and except for the water the products are soluble in benzene. Nine-tenths of the products are soluble in alkali, and half of this material can be reprecipitated by acid.

It has already been noted that pure cellulose [43] changes into *levo*-glucosan by vacuum distillation. A thick oil, boiling point (15 mm.) 200-300°, passes over, which represents 45 percent by weight of the cellulose. This is largely *levo*-glucosan. On standing, part of the oil crystallizes (melting point 179.5°). Inorganic impurities [44] in cellulose are detrimental to a good yield of *levo*-glucosan. As the water soluble parts are removed from the cellulose, the yield of *levo*-glucosan changes from 0 percent to 28 percent. Venn obtained a 38 percent yield by treatment first with 1.5 percent solution of sodium hydroxide, followed by a 1 percent solution of hydrochloric acid.

Vacuum distillation of methyl cellulose [45] has led to interesting results. Reasoning by analogy from cellulose, Reilly believed that if the atomic groupings in *levo*-glucosan pre-exist in cellulose, then by vacuum distillation methyl cellulose should give methyl *levo*-glucosan. Such was found to be the case.

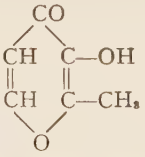
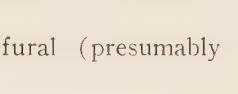
Erdmann and Schaefer [46] heated kilogram lots of starch-free filter paper in a copper retort of 7-liter capacity until volatile products failed to come over; duration of the heating, 2 hours. Analysis of the gaseous products revealed the following relationships: carbon monoxide 65.5 percent, methane 19.0 percent, hydrogen 11.5 percent, nitrogen 2.4

[41] Bain, *J. Soc. Chem. Ind.* **46**, 193T (1927).
[42] Fischer and Schneider, *Ges. Abhandl. Kenntn. Kohle* **3**, 287 (1919); *Chem. Abstracts* **14**, 2081 (1920).
[43] Pictet and Sarasin, *Compt. rend.* **166**, 38 (1918).
[44] Venn, *J. Textile Inst.* **15**, 414T (1924).
[45] Reilly, *Helv. Chim. Acta* **4**, 616 (1921).
[46] Erdmann and Schaefer, *Ber.* **43**, 2398 (1910).

percent, oxygen 0.9 percent, carbon dioxide 0.2 percent, and other hydrocarbons 0.5 percent. In two series of 9 distillations each (therefore, 9 kg. of paper), there was collected 3810 and 3750 grams of a tarry-water distillate; and 425 and 450 grams (4.7 and 5 percent respectively) of a tar. The brown, aqueous solution possessed an intense odor; it reacted strongly acidic; it gave a dark violet ferric chloride reaction; and it reduced ammoniacal silver solution. About 406 grams (from each 9 kg. of paper) could be extracted by ether; this gave the following four fractions by distilling in a vacuum of 0.002 mm.

(1) *The fraction having a boiling point (0.002 mm.) of 10-56°.* This weighed 79 grams or comprised 19.4 percent of the extract.

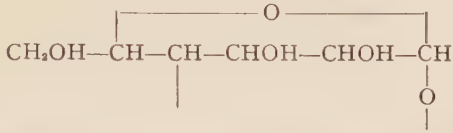
(2) *The fraction boiling from 56-76°.* This weighed 98 grams or was 24.1 percent of the extract. Furfural was found to be an essential component of these two fractions. Small amounts of formaldehyde had been previously identified in the original watery distillate.

(3) *The fraction which boils from 76-110°.* This weighed 64 grams or was 15.8 percent of the extract. It was an orange, viscid oil from which crystals of maltol,  , separated in small amounts (2.5 grams from 9 kg. of filter paper). Maltol gives an intense violet coloration with ferric chloride. The third fraction was also shown to contain hydroxymethyl furfural (presumably ), which was isolated as its semioxamazone, R—CH=N—NH—CO—CONH$_2$. Eleven grams of this latter derivative was isolated from 43 grams of the third fraction. The remaining important product in this fraction was γ-valerolactone. After the removal of the maltol and hydroxymethyl-furfural, the remaining liquid distilled without pyrolysis at atmospheric pressure. For the most part it distilled between 205-225°, and the lactone made up one-third to one-fourth of this portion. It was extracted by water.

(4) *The fraction boiling from 110-230°.* This weighed 65 grams or was 16 percent of the extract. It was a viscid, red-brown sirup. The residue weighed 100 grams (24.6 percent), and it resembled asphalt. It would be expected that the fourth fraction should contain *levo*-glucosan to a large extent, but this was not investigated.

At this point, it may be helpful to indicate the structure of the

glucose nucleus which exists in the cellulose molecule. As with starch, this is still an open question, but the following [47] is considered to be most in keeping with the facts:



Comparison with the similar formula for starch (p. 277) reveals the close relationship of the two. Since *levo*-glucosan is an important pyrolytic product of both starch and cellulose, it is apparent that the atomic groupings in *levo*-glucosan cannot pre-exist in both starch and cellulose. Possibly it does not pre-exist in either, but in any event, the relationship between the structure of *levo*-glucosan and both starch and cellulose must be a very close one. Fischer and Tropsch have confirmed [48] the observation of Pictet and Sarasin that *levo*-glucosan may be prepared by vacuum-distilling pure cellulose. From 100 grams of cellulose, there was formed a distillate of 72-77 grams, 15.8 grams of which was *levo*-glucosan; the residue of coke weighed 14-16 grams; and the gases and loss were 8-12 grams.

At 340°, cellulose eventually gives a coal-like residue.[49] If this residue is highly compressed at this temperature (5000 kg./sq. cm.) a product resembling anthracite results. This coal-like residue has also been noticed by Waterman,[50] who heated cotton cellulose under pressure at 225-450°. After 2 hours at 225°, the black residue resembled coal (carbon, 48.9 percent and hydrogen, 6.1 percent). This residue weighed 85 percent of the original cellulose. The analysis of the residue after one hour's heating at 300° is as follows: carbon, 71.0 percent and hydrogen, 5.2 percent). At 450°, it is 85.7 percent carbon and 5.0 percent hydrogen. The products of the reaction at 300° are stated to be mainly carbon dioxide and water, and at 450°, carbon dioxide, water, carbon monoxide, methane and other paraffins. Except for a larger amount of hydrocarbons, no other effect was apparent when a hydrogen atmosphere was maintained. This is also the observation [51] of Fierz David and Hannig, who reported that the dry distillation of cellulose is uninfluenced by the presence of hydrogen (unless catalysts are present) even up to 300 atmospheres pressure.

The experiments in which high pressures are used are interesting to

[47] Irvine, *Chem. Reviews* **4**, 224 (1927).
[48] Fischer and Tropsch *Chem. Zentr.* **1923**. III, 1400; *Ber.* **56**, 2418 (1923).
[49] Bergius, *Z. Elektrochem.* **19**, 858 (1913).
[50] Waterman and Perquin, *Rec. trav. chim.* **45**, 638 (1926).
[51] Fierz David and Hannig, *Helv. Chim. Acta* **8**, 907 (1925).

study in comparison with the experiments which were performed at low pressures. Fierz David and Hannig heated 500 grams of pressed cellulose at 140 atmospheres. In 30 minutes the temperature had reached 180°, and in 90 minutes, 250°, at which temperature an exothermic reaction was apparent. In 10 minutes, this caused the pressure to change from 190 atmospheres to 254 atmospheres, the temperature advancing to 280°. The first condensate was a yellowish-brown, watery liquid, and then a few drops of a brown oil. At 300°, the distillate became more tarry, and finally at about 400° a black, tough, thick tar came over. During the three-quarters of an hour from 280-400°, the pressure was kept between 40 and 60 atmospheres. There was a residue of 159 grams of cellulose charcoal, and a total distillate of 194 grams (152 grams of watery liquid having an acidity of 6.3 percent; 38 grams of tar; 4 grams condensed at — 80°). The gases and loss amounted to 147 grams. The 38 grams of tar was separated into

(1) Phenols, 7.6 grams; phenol, cresols, and probably xylenol and guaiacol.
(2) Acids, 5.2 grams; from formic to valeric acids.
(3) Neutral substances, 15.5 grams; ketones, including acetone, methylethyl ketone and cyclopentanone (most of the ketone content was in the water soluble portion), furan and its homologs (methyl furan to hexyl furan at least).

Comparative experiments [52] on the pyrogenic decomposition of cellulose, rice starch and sugar from an iron retort have been reported by Bantlin, and Costa [53] has heated cellulose in neutral paraffin oil. In the latter case, cellulose starts to give gaseous products at 260-270°; the evolution is greatest at 280-290°, and the gas evolution ceases at 300-310°, leaving the cellulose residue of a brown-black color. The gases are chiefly carbon dioxide and steam. A cellulose, carbon 44.42 percent, hydrogen 6.22 percent and oxygen 49.36 percent, gives the following residue: at 300°, carbon, 69.87 percent; hydrogen, 5.53 percent; oxygen, 24.6 percent; and at 365°, carbon, 83.11 percent; hydrogen, 6.40 percent; oxygen, 10.49 percent. These high-temperature residues, it is again pointed out, resemble coals.

The fact that cotton gives a higher yield of *levo*-glucosan than other cellulosic materials has an explanation [54] in that cotton contains a minimum amount of β-cellulose (alkali-soluble matter, precipitated by acids; α-cellulose is alkali-insoluble). In fact, β-cellulose fails to give *levo*-glucosan by vacuum distillation, and substances such as esparto cellulose which contain a fairly high amount of β-cellulose give low yields of *levo*-glucosan on distillation. Distillation of β-cellulose gives more gases

[52] Bantlin, *J. Gasbel* **57**, 32 (1913); *Chem. Abstracts* **8**, 1344 (1914).
[53] Costa, *Ann. chim. applicata* **16**, 647 (1926); *Chem. Abstracts* **21**, 1707 (1927).
[54] Mutti and Montalti, *Ann. chim. applicata* **17**, 188 (1927); *Chem. Abstracts* **21**, 2381 (1927).

than α-cellulose, a smaller percentage of tar, about the same quantity of aqueous liquor, and a coke-like residue. In both cases, the aqueous liquor contains aldehydes, ketones, furfural and pyroligneous substances. Only in the case of the α-cellulose, however, is there any *levo*-glucosan.

Wood.

The subject of wood distillation has already been treated in detail in two monographs [55] of this series. Furthermore, wood is not a compound. In this chapter, therefore, it will only receive passing mention.

The substances which have been identified among the products of wood distillation may be arranged, for the most part, in a few groups of related compounds. Much of the accurate knowledge [56] on this subject is due to the work of Klason. The groups are enumerated below.

1. *Acids;* formic to caproic, especially acetic acid. Also, furoic, angelic, lignoceric acids, and valerolactone. For different woods, the total acid, calculated as acetic acid, varies between 4.3 and 6.8 percent. In vacuum distillation processes, formic acid may be formed in quantities as high as 35 percent of the acetic acid, but in ordinary distillation at atmospheric pressure, it varies from 10 to 20 percent of the acetic acid. Only these two acids appear to be formed in appreciable amounts.

2. *Alcohols;* especially methanol and allyl alcohol, but also *iso*amyl and *iso*-butyl alcohols, and buten-3-ol-2. The methanol content is usually between 1.3 and 2 percent.

3. *Esters;* formed by interaction of the above acids and alcohols.

4. *Ketones;* acetone in particular, and also its homologs. Besides these there are small quantities of cyclopentanone, methyl cyclopentanone, and diacetyl. The acetone is not a primary product of the distillation, but is formed secondarily from the acetic acid first produced. No doubt the homologs of acetone have a similar history.

5. *Aldehydes;* formaldehyde, acetaldehyde, methylal and dimethyl acetal, valeric aldehyde, furfural and methyl furfural. The pentosans are obviously the source of the furfural and other furan products (homologs of furan, of which there are several).

6. *Phenols* and *phenol methyl ethers,* mostly methyl ethers of di- and triphenols. The total quantity of this group makes up only about 1 percent of the wood distilled. These substances come largely from the lignin.

7. *Ammonia, methyl amine, pyridine* and *methyl pyridine,* which constitute less than 0.2 percent of the total.

8. *Toluene, m-xylene, melene,* etc.

9. *Gases;* the yields of carbon dioxide, carbon monoxide and methane vary with the maximum temperature of distillation, but at 350-400° the yields from hardwoods are about 8, 4 and 1.5 percent, respectively.

10. *Water;* the yield of which varies from 22.3 to 27.8 percent.

11. *Charcoal.* The charcoal may represent 30-45 percent of the weight of the wood, depending on the wood, and on the maximum temperature.

Cellulose, pentosans, lignin and other substances which are present in wood all contribute somewhat to the final result. Usually the yield

[55] Hawley, "Wood Distillation," New York, Chemical Catalog Co., 1923; Hawley and Wise, "The Chemistry of Wood," *ibid.,* 1926.

[56] Klason, von Heidenstam and Norlin, *Arkiv Kemi. Mineral. Geol.* 3, 1-34 (1908); *Z. angew. Chem.* 25, 1205 (1909); 27, 1252 (1910). Klason, *J. prakt. Chem.* [2] 90, 413 (1914); Hawley, *loc. cit.,* p. 65. Hawley and Wise, *loc. cit.,* p. 199.

of charcoal from wood is slightly higher than from cellulose, and the same is true regarding the yields of methane and of tar. Furthermore, wood gives rise to a much greater acetic acid content than cellulose. Almost no methanol is produced by the pyrolysis of cellulose, and all evidence seems to indicate lignin as the source of the wood alcohol. The acetic acid comes partly from the cellulose and partly from the lignin, but most of it appears to come from the pentosans. The pentosans also appear to be the precursors of the formic acid.

Comparative vacuum distillations of cellulose[57] (a bleached commercial pulp), wood and lignin give values for wood which usually lie between cellulose and lignin. With the volatile acids, however, the values for wood are much higher than for cellulose or lignin. This, as Hawley and Wise point out, may be due to the presence of pentosans in wood, and their absence, or near absence, in either paper pulp or lignin.

The possibility that *levo*-glucosan may be a product of wood distillation at low pressures has been investigated by Mutti and Montalti.[54] Apparently, it is not produced from wood under the conditions of ordinary vacuum distillation, nor is it produced from wood that has been previously treated with hot 1 percent sodium hydroxide solution. However, with wood which has been treated with moist chlorine gas (either with or without the previous NaOH treatment), *levo*-glucosan is formed in yields varying from 0.34 percent to 2.70 percent.

Klason's work on the distillation of wood[58] in a cathode-light vacuum gives results which are very much different from ordinary distillation. Instead of a 10 percent yield of tar, there is a 43.6 percent yield. This tar differs from ordinary wood tar in its light color, transparency and hard consistency. At about 275°, the temperature of decomposition for wood itself, it decomposes exothermally into water, carbon dioxide, tar coke, and ordinary tar. The composition of this tar was not studied but Hawley[59] suggests that *levo*-glucosan may be present.

The effect of moderate heat,[60] 80-100°, for periods up to 530 hours, on cloth, paper, wood, cork, tannic acid, starch, albumin and linseed oil has been outlined by Knecht. Corn flakes[61] undergo a conspicuous "toasting" in 5 minutes at 193°; probably this is a dextrinizing process.

[57] Fischer and Tropsch, *Ber.* **56**, 2418 (1923).
[58] Klason, *J. prakt. Chem.* **90**, 413 (1914).
[59] Hawley, "Wood Distillation," New York, Chemical Catalog Co., **1923**, p. 55.
[60] Knecht, *J. Soc. Dyers and Colourists* **36**, 195 (1920); *Chem. Abstracts* **14**, 2860 (1920).
[61] Buchwald and Kühl, *Z. angew. Chem.* **39**, 1073 (1926).

PENTOSANS.

Heuser [62] has investigated the products of the pyrolysis of xylan. Between 160-315°, it forms 18 percent of gas, 31.5 percent of residue, 43.8 percent of aqueous distillate and 6.7 percent of tar. Seventeen percent of the distillate is acetic acid, and nearly 14 percent furfural. Some allyl alcohol is also present. By conducting the distillation (xylan) at 1 mm. up to 300°, there is formed 20.2 percent of a sirup from which crystals, $C_5H_6O_3$, slowly separate. These melt at 206°. It may be that these crystals are the pentose analog of *levo*-glucosan, a hexose derivative formed by distilling starch or cellulose.

The dry distillation of rice chaff [63] and oats chaff begins at 120° and is complete at 400°. Most of the decomposition is between 200-300°. There is formed 20 percent of gas, 41 percent of a carbonaceous residue, 33 percent of an aqueous distillate which contains 4 percent acetic acid, and 6 percent oil. Nearly one-third of this oil boils above 270°, and this portion is very fluid. It consists largely of phenols, fatty acids and anhydrides of hydroxy-acids.

COAL.

DISTILLATION OF COAL.

As with wood, only the briefest possible treatment of this vast subject is permissible in a book of this nature. As is well known, coal tar furnishes the chief source for aromatic compounds. Benzene, toluene, xylene, naphthalene, anthracene, pyridine, quinoline, phenol and cresol are the best known compounds which may be obtained directly. Other compounds which have less commercial value, and in fact which are frequently detrimental because of the difficulty of their removal from the substances with which they are mixed, are thiophene, thionaphthene,[64] quinaldine, phenanthrene, pyrene, chrysene, indene and cumarone.

It has already been pointed out that some of the more complex products (p. 100) are undoubtedly formed as the results of secondary reactions. Thus, there is the formation of phenanthrene from cumarone and benzene; chrysene from cumarone and naphthalene, or from indene; naphthalene from simpler hydrocarbons. It is particularly pertinent to note that neither benzene nor its homologs can be detected in the liquid products of distillation of coal, when the distillation is carried out in

[62] Heuser and Scherer, *Brennstoff-Chem.* **4**, 97 (1923); *Chem. Abstracts* **17**, 2954 (1923).
[63] Marcusson and Picard, *Chem. Ztg.* **47**, 585 (1923); *Chem. Abstracts* **17**, 3243 (1923).
[64] Weissgerber and Kruber, *Ber.* **53**, 1551 (1920).

a vacuum.[65] Occluded gases are removed up to 150-200°, and at 200° water is evolved copiously and this continues to come off until 450°. At about 350° gases are rapidly evolved and a viscid oil distils. When bituminous coals are distilled in a vacuum (5-40 mm.) at 430°, 65 percent of the weight of the coal distils as oils or tars; about half of this is pitch with a boiling point above 300°. Between 40 and 45 percent of the other half is olefine hydrocarbons; 40 percent naphthenes, with a small contamination of liquid paraffins; 12-15 percent cresols and xylenols; and 7 percent aromatic compounds, considered to be homologs of naphthalene.

Wheeler postulated a preferential decomposition of the resinic constituents of coal over the cellulosic, but Drakeley could not agree with this. The analysis of a gas from coal at 400-600° and 15-20 mm. is: hydrogen, 22.8 percent; paraffins, 59.3 percent; carbon monoxide, 8.7 percent; ethylenes, 5.1 percent; and carbon dioxide, 4.1 percent. At 800-900°, the relative volumes of hydrogen and of paraffins are nearly reversed: hydrogen, 56.5 percent; paraffins, 21.7 percent. The gases from samples of anthracite [66] in a vacuum at 1000-1200° are over 90 percent hydrogen, and Lebeau considered this as a good potential source of hydrogen for the ammonia synthesis. At ordinary pressures, the following stages are given by Savage [67] in the carbonization of coal; softening at 150-200°, paraffins evolved at 230°, more gases at 400°, a more rapid oil elimination at 430-530°, and between 820-1680° only a carbon residue is left which fuses to great hardness. At the low temperatures, the durain portion [68] of coal appears to decompose more easily than the vitrain, but above 350° both decompose similarly.

A hypothesis that coal originated from the lignin of wood and not from the cellulose was proposed by Fischer and Schrader.[69] These investigators pictured lignin as having an aromatic structure, with acetyl and methoxyl groups. The methoxyl content in the transformation, although increasing at first with increasing age, due to the destruction of most of the cellulose to carbon dioxide and water by bacterial action, must eventually decrease, due to its change into humic acid, which is phenolic. Oxidation or polymerization of the latter forms the alkali-insoluble humin which changes eventually into lignite and coal by the splitting off of water, carbon dioxide and possibly methane. The fact that cellulose yields phenol almost exclusively on distillation, whereas

[65] Burgess and Wheeler, *J. Chem. Soc.* **97**, 1917 (1910); **99**, 649 (1911); **103**, 1704 (1913); **105**, 131 (1914); Jones and Wheeler, *ibid.* **105**, 140, 2562 (1914); Drakeley, *ibid.* **121**, 221 (1922); Pictet and Bouvier, *Ber.* **46**, 3342 (1913); *Compt. rend.* **157**, 779, 1436 (1913).
[66] Lebeau, *Compt. rend.* **177**, 456 (1923).
[67] Savage, *Chem. Met. Eng.* **19**, 579 (1918).
[68] Uchida, *Fuel Science Practice* **5**, 221 (1926).
[69] Fischer and Schrader, *Brennstoff-Chem.* **2**, 37 (1921).

coal yields principally the higher homologs, is cited as further indication of the absence of cellulose derivatives in coal.

In comparative runs on the distillation of lignin and of cellulose, the same authors point out that lignin gives less than half the quantity (13/33) of water, and nearly half the quantity of tar (12/22) produced by cellulose, but that it yields over twice the amount (57/25) of semi-coke. The gases evolved in both are nearly equal (34/37). Half of the tar from lignin is phenolic or acidic, as contrasted with the 17 percent value in the tar from cellulose.[70] Wood stands intermediate between lignin and cellulose.

The results of Pictet and Gaulis [71] on the distillation of lignin also supports Fischer and Schrader's hypothesis. Fifteen percent of oil, which alone was studied in detail, 21 percent of an aqueous-acid solution, and 52 percent of coke and ash result when the distillation is performed at 350-390° under 5 mm. pressure in a copper tube. Eleven percent of the original oil (2 percent of the original lignin) resists extraction from an ether solution by a 10 percent sodium hydroxide solution. Eight hydrocarbons were isolated from this oil, three of which were identical with those produced in a similar manner from coal. It must not be forgotten, however, that this represents but 2 percent of lignin, and 3 percent of coal.

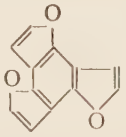
By oxidizing lignin at 200°, Kürschner [72] obtained a sublimate of vanillic acid, in 55-60 percent amounts. There was a caramel-like residue. On this basis, it was suggested that lignin is a glucoside, since tannins, which are known to be glucosides, yield a sublimate of tannic acid when they are treated similarly. Vanillic acid is 3-methoxy-4-hydroxybenzoic acid.

Marcusson disagrees with Fischer and Schraeder's hypothesis that only the lignin contributes to the formation of coal, and thinks that cellulose also contributes. He suggests [73] that the latter is transformed, during the process of decay, by hydrolysis and oxidation into oxycellulose and pectin constituents. The glucuronic acid, a component of oxycellulose, changes easily into humic acids which are further transformed into coal. At least, humic acids are generally acknowledged as a precursor of coal. Schwalbe and Schepp [74] also indicate that lignin as well as cellulose takes part in coal formation.

Marcusson [75] believes that the furan nucleus is an essential part of

[70] Fischer and Schrader, *Ges. Abhandl. Kenntn. Kohle* **5**, 106 (1920); Fischer and Tropsch, *Ber.* **56**, 2418 (1923); also *Chem. Abstracts* **18**, 2600 (1924).
[71] Pictet and Gaulis, *Helv. Chim. Acta* **6**, 627 (1923).
[72] Kürschner, *Brennstoff-Chem.* **6**, 117, 177, 188 (1925).
[73] Marcusson, *Z. angew. Chem.* **39**, 898 (1926).
[74] Schwalbe and Schepp, *Ber.* **58**, 2500 (1925).
[75] Marcusson, *Ber.* **58**, 869 (1925).

humic acids, peat and coal, and suggests that three furan nuclei may condense to a 6-membered ring system:



He relates how the brown humic acids are formed from furfural in 1 percent sodium hydroxide and oxygen, conditions so mild that it is unnecessary to assume an intermediate rupture of the ring. With such a nucleus it is not difficult to understand why dry distillation of anthracite yields cumarone, identified as cumarone resin, up to 40 percent of the 155-185° fraction of the tar. He states that by heating humic acids to 250° in the absence of air (in mineral oil), pyrohumic anhydride and humic ketones are formed which are constituents of peat. Also, the natural transformation of peat into anthracite may be imitated in the laboratory by heating under pressure.

Low-Temperature Carbonization of Coal.

Ordinary coal carbonization processes are high-temperature ones, usually about 950-1300°. It is obvious, therefore, that many of the products found in ordinary coal tar are formed as a result of secondary decompositions of the primary liquid products. It would seem that more liquid and fewer gaseous products would be formed if the carbonization were carried out at lower temperatures. Such has been found to be the case, and in recent years a considerable amount of work has been done on this problem. One of the major difficulties in large scale work is uniform heating of the coal in the retort. In general, however, low-temperature processes operate at 500-600° and never above 750°.

Parr and Layng [76] found that at 300-400° an exothermic reaction sets in which supplies heat to the interior of the retort charge. Illingworth noted [77] that temperatures as low as 450° tended to destroy the constituents of coal which were soluble in pyridine, namely, the β-cellulosic and the resinic. The β-cellulosic appeared to be destroyed more rapidly.

By observing that the coal tar from low-temperature processes consists essentially of phenols and of hydrocarbons similar to petroleum, but without admixture of aromatic hydrocarbons, Fischer and Schrader [78] concluded that the aromatic hydrocarbons found in high-

[76] Parr and Layng, *Ind. Eng. Chem.* 15, 591 (1923).
[77] Illingworth, *J. Soc. Chem. Ind.* 39, 111T (1920).
[78] Fischer and Schrader, *Brennstoff-Chem.* 1, 4 (1920).

temperature coal tar must have come by reduction of the phenols, since petroleum hydrocarbons can give but a small percentage of them. In support of this contention, it was found that when *o*-cresol and hydrogen were passed through a tinned-iron tube at 750° the aromatic hydrocarbon formation was 72 percent, as compared to 7 percent from a hexane-hydrogen mixture.

Gaseous hydrocarbons,[79] formed from the low-temperature carbonization of a resinous, non-coking coal, were analyzed by Frey and Yant. The conditions of heating were about 700° with superheated steam, which of course should scarcely be regarded as an inert atmosphere. They found no oxygen, acetylene, methyl acetylene, allene, cyclopropane, methyl cyclopropane, cyclobutane, dimethyl acetylene or methyl allene. About 1 percent or less of the following were reported: ethylene, propylene, propane, butene-1, butene-2, butane, *iso*butane, butandiene-1,3, nitrogen and hydrogen sulfide, but the following were the more prominent components of the mixture: methane, 32.4 percent; hydrogen, 33.5 percent; carbon dioxide, 11.0 percent; carbon monoxide, 11.7 percent; and ethane, 3.8 percent. The water-gas reaction may have contributed largely to the amounts of hydrogen and carbon oxides. Interesting articles in which low-temperature carbonizing methods and results are discussed are indicated [80] below.

In passing, it may be mentioned that one of the characteristics of low-temperature tar and tar oils is the red color which they impart to any water [81] that has come in contact with them, particularly if such water is slightly alkaline. It has been found that the material in the tars that is responsible for this red color is a mixture of homologs of catechol, but not catechol itself. Catechol, *o*-hydroxyphenol, is a product isolable in the distillation of certain vegetables and of catechin.

[79] Frey and Yant, *Ind. Eng. Chem.* **19**, 488 (1927); **19**, 21 (1927).
[80] Tupholme *Chem. Met. Eng.* **30**, 1019 (1924); Curtis and Geldard, *ibid.* **28**, 61 (1923); Morrell and Egloff, *Ind. Eng. Chem.* **17**, 473 (1925); Brownlie, *ibid.* **19**, 39 (1927).
[81] Burke and Caplan, *Ind. Eng. Chem.* **19**, 34 (1927).

CHAPTER 12.

AMINES.

Primary Amines.

The ammonia system of compounds needs no introduction (see p. 21). The behavior of primary amines and primary alcohols is so similar in many reactions, that it would be surprising if the similarity failed to extend to the reactions of pyrolysis. Were the behavior of amines and alcohols qualitatively analogous in this respect, ethyl amine should in part be deammonated to ethylene and ammonia, and in part be dehydrogenated to acetonitrile, through an intermediate aldimide, $[CH_3—CH{=}NH]$. Thus,

$$CH_3—CH_2OH \begin{cases} \nearrow\ CH_2{=}CH_2 + H_2O \\ \searrow\ CH_3—CHO + H_2 \end{cases}$$

and

$$CH_3—CH_2NH_2 \begin{cases} \nearrow\ CH_2{=}CH_2 + NH_3 \\ \searrow\ [CH_3—CH{=}NH] + H_2 \end{cases}$$

$$\downarrow$$

$$CH_3—C{\equiv}N + 2H_2.$$

Actually, acetonitrile, hydrogen, ethylene and ammonia appear to be the primary products of the pyrolysis. The very familiar equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24\ \text{Cal.},$$

is a reminder that at temperatures which are sufficiently elevated, ammonia is decomposed into its elements. At 700°, the transformation into the elements is almost complete. It is reasonable, therefore, to find that nitrogen and hydrogen gases accompany the production of ammonia from amines at 500°, and to find only the decomposition products of ammonia at 1000°.

Ethyl amine has been pyrolyzed[1] at 500°, 700° and 1000° over kaolin. *n*-Propyl amine has been similarly investigated at 700°. In this work, the products of decomposition were first passed through a U-tube surrounded by a freezing mixture, then through a wash bottle containing standard acid, and finally the gaseous products were collected in

[1] Upson and Sands, *J. Am. Chem. Soc.* **44**, 2306 (1922).

TABLE XXXII. *Ethyl Amine.*

Temperature °C.	Carbon in Furnace Percent	U-tube NH4CN —NH2 (amine)	U-tube NH4CN HCN	U-tube RCN	Acid Wash Bottle —NH2	Acid Wash Bottle Amine	Acid Wash Bottle HCN	Gases C2H4	Gases H2	Gases N2	CnH2n+2 C	CnH2n+2 H	Total Percent
		Percent	Percent		Percent	Percent		Percent	Percent	Percent	Percent	Percent	
500	1	5.1	...	28.3	15.9	10.2	...	14.8	1.9	2.6	4.3	1.0	84.9
700	6.5	6.4	6.4	22.6	13.3	...	0.5	7.2	2.9	1.0	17.4	4.2	88.4
1000	5.6	...	...	trace	...	...	...	trace	5.3	33.2	26.9	6.0	77.0
					Propyl Amine								
700	7.2	4.3	4.9	15.9	9.3	...	1.7	*	2.9	4.6	14.5	3.4	78.3

* = 3.0 percent ethylene and 6.4 propylene.
... represents a percent yield of 0.0.

a container over mercury and analyzed. The cold U-tube removed unchanged amine, ethyl- or propyl-cyanide, and ammonium cyanide, whereas the standard acid removed ammonia and any uncondensed amine. It appears that at 500°, considerable amine was collected by the acid, but none whatever at 700° or above.

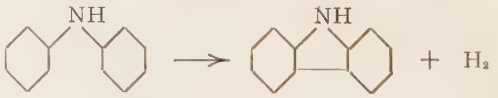
Results for the percentage by weight of the decomposition of both amines based on the weight of amine taken are given in Table XXXII.

A study of these results shows that the major primary reaction is a pyrolysis into acetonitrile and hydrogen, and that a lesser reaction, although quite large also, is a pyrolysis into ethylene and ammonia. As would be anticipated, the secondary reactions grow in importance with increasing temperature, and at 1000°, essentially nothing was found save hydrogen, nitrogen and paraffin hydrocarbons. The astonishing feature, however, is that the hydrocarbon mixture appears to be largely *butane*, based on vapor density measurements. It has repeatedly been demonstrated that the only paraffin with a reasonable degree of stability at 1000° is methane. The data indicate that butane is present to the extent of 32.9 percent by weight (26.9 + 6.0); if this value is calculated in terms of mols, it is found to represent about a 50 percent yield of butane. It would seem that with such a high yield as this, butane should have been condensed in the freezing mixture (butane boils at + 1°) but none, apparently, did so.

Upson's premise is that ethyl amine decomposes primarily into ammonia and "ethylidene", after which the *n*-butane "must have been formed by the union of two ethylidene radicals and two atoms of hydrogen as in the Würtz reaction". It would seem that a reaction that proceeds apparently normally at 500° or at 700°, but so abnormally at 1000° should be supported by better evidence than vapor density measurements.

Müller has reported [2] that ethyl amine gives methane and hydrogen cyanide at 1240°. Other simple primary aliphatic amines seem not to have been studied.

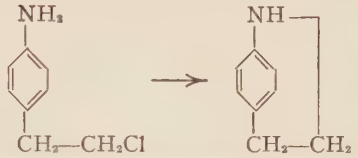
Aniline gives poor yields of carbazole [3] when it is passed through a hot tube. Diphenylamine, however, gives good yields.



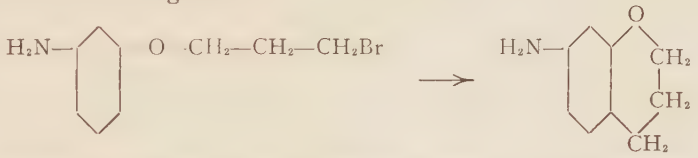
[2] Müller, *Bull. soc. chim.* [2] **45**, 439 (1886).
[3] Graebe, *Ann.* **167**, 125 (1873); **174**, 177 (1874).

α-Aminothiophene (thiophenin) may be distilled [4] in a high vacuum, but at ordinary pressure it undergoes pyrolysis into ammonia, hydrogen sulfide and a carbonaceous residue.

The pyrolysis of *p*-β-chloroethyl-aniline [5] is of unusual interest, inasmuch as the product which is stated to be formed, namely, dihydro-*p*-indole, is one of the very few cases of *para*-ring-closure through a benzene nucleus:



p-γ-Chloropropyl-aniline does not behave in this manner as it fails to form *p*-tetrahydroquinoline. Wilson and Adams [6] were not able to isolate any definite product by heating *p*-aminophenol-β-bromoethyl ether, $H_2N—C_6H_4—O—CH_2CH_2Br$. With *m*-γ-bromopropoxy-aniline, heating does produce a change in which hydrogen bromide is eliminated, but the resulting compound is an amino-chromane. There is absolutely no evidence of *meta* ring closure.



Carbazole is formed when 2-aminodiphenyl [7] is distilled over hot chalk. 2,2′-Diaminodiphenyl is extremely resistant [8] to heat, but it pyrolyzes somewhat into anthracene and tars. A little resinous matter is similarly isolable from the 4,4′-derivative, $H_2N—C_6H_4—C_6H_4—NH_2$, but rather curiously there was formed some $H_2N—C_6H_4—CH_2—CH_2—C_6H_4—NH_2$.

Secondary and Tertiary Amines.

Dimethylamine [9] pyrolyzes at 800-1000° into hydrogen cyanide, methane and hydrogen, and the conversion of trimethylamine into prussic acid and methane is nearly quantitative:

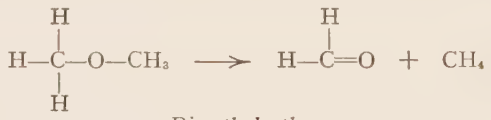
$$(CH_3)_3N \longrightarrow HCN + 2CH_4.$$

[4] Steinkopf, *Ann.* **403**, 19 (1914).
[5] von Braun *Ber.* **45**, 1274, 2512 (1912).
[6] Wilson with Adams, *J. Am. Chem. Soc.* **45**, 530 (1923).
[7] Blank, *Ber.* **24**, 306 (1891).
[8] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).
[9] Müller, *Bull. soc. chim* [2] **45**, 439 (1886).

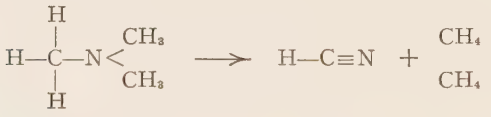
Diethylamine and triethylamine are both reported to yield prussic acid and methane at about 1200°, but there is also much carbonization.

In the pyrogenic decomposition [10] of ethyl aniline, small amounts of indole are formed, but only traces of indoles are formed from monoethyl aniline. Somewhat better yields come from methylethyl aniline or diethyl aniline. Still better yields are apparent with dimethyl *o*-toluidine, and with *dicthyl o-toluidine,* about 3-5 percent of pure indole results (see p. 466). Indole is found in coal tar (3-5 percent of the 220-260° portion), and of course coal tar is also of pyrogenic origin.

The products from dimethylaniline,[11] as it is passed through a glowing tube are benzonitrile, ammonia, benzene, hydrogen cyanide and gases which are probably hydrogen and methane. This is somewhat comparable to the case of trimethylamine which has just been given. An analogy is permissible between trimethylamine and dimethyl ether, since they are both "ethers" of their respective systems.



Dimethyl ether



Trimethylamine (Trimethyl-ammonoether)

It is apparent that the carbon atoms in the ether have been simultaneously oxidized and reduced, and the same condition exists in the amine. On this basis, dimethylaniline might be compared with anisole, but the observed products of pyrolysis are not quite as comparable. Anisole, $C_6H_5OCH_3$, gives phenol and ethylene. The comparable reaction with dimethylaniline would lead to aniline and ethylene, but apparently this does not occur. Instead, dimethylaniline pyrolyzes much in the manner of trimethylamine although not quite as smoothly. The benzonitrile which is formed in this reaction [12] has a similar origin to the benzonitrile from methyl-diphenyl-amine; the mechanism of the two reactions is probably similar:

[10] Baeyer and Caro, *Ber.* **10**, 692, 1262 (1877).
[11] Nietzki, *Ber.* **10**, 474 (1877).
[12] Graebe, *Ann.* **174**, 184 (1874).

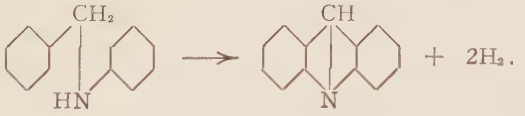
Lesser amounts of diphenylamine, carbazole, methane and nitrogen are also formed.

On p. 228 it was mentioned that phenyl-allyl-amine behaved in much the manner of phenyl allyl ether towards heat. In both cases, there is a migration of the allyl group from the oxygen or the nitrogen to a nuclear carbon atom. With phenyl allyl ether, the product of the rearrangement is *o*-allyl phenol:

$$C_6H_5—O—CH_2—CH=CH_2 \longrightarrow C_6H_4\begin{<}{OH}\\{CH_2—CH=CH_2}\end{}.$$

The comparable reaction with *N*-allyl aniline would be a rearrangement into *o*-allylaniline. Whether or not this is the exclusive compound of the reaction has not been determined with certainty, but at least it is known [13] that there is a change from a secondary amine to a primary amine by refluxing for 9 hours. During this time the temperature of refluxing increases from 205° to 230°. Similarly, *diallylaniline*, $C_6H_5N(CH_2CH=CH_2)_2$, changes its boiling point from 243° to 268° in the course of 10 hours, and the resultant mixture of products contain primary, secondary and tertiary amines, indicating some unchanged material and a rearrangement of one or both allyl groups to the nucleus.

The fact that carbazole is a product of the pyrolysis of diphenylamine has already been mentioned. In addition, it has been established [14] that prussic acid is also a product of this reaction. No carbazole derivative is formed, however, from dinaphthylamine; instead, ammonia is evolved and naphthalene is also formed. Meyer and Hofmann found that benzylaniline gives such a good yield of acridine by pyrogenic methods that it is recommended as a superior method of preparation:



Benzyl aniline is comparable in structure to phenyl benzyl ether (pp. 202 and 222); the latter substance has not been subjected to red heat, but it has been studied at boiling temperature. 9,10-Dihydroacridine is partially dehydrogenated [15] into acridine at 300° in a sealed tube.

Dibenzylamine is scarcely affected if it is distilled rapidly (above 300°), but in a gradual distillation [16] it is largely changed. Tribenzylamine undergoes pyrolysis by distillation, and the products seem identical throughout to those from dibenzylamine. In each case, the volatile

[13] Hurd and Greengard, unpublished results.
[14] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916); Pictet and Gonset, *Chem. Zentr.* **1897**, I, 414.
[15] Graebe and Caro, *Ann.* **158**, 279 (1871).
[16] Brunner, *Ann.* **151**, 135 (1869).

products are toluene, ammonia, dibenzyl and toluylene ($C_{14}H_{12}$). The residue, which represents about half of the original amine, contains lophine.[17] By dissolving the residue in alcohol and adding hydrogen chloride, two salts of uncertain structure may be isolated. They are $(C_7H_7)_4NCl$, melting point 230°, and $(C_7H_6)_3H_3N_3HCl$, melting point 162-163°.

There is indirect evidence to show that benzohydrylamine, $(C_6H_5)_2CHNH_2$, undergoes pyrolysis into the tertiary amine, $((C_6H_5)_2CH)_3N$, and ammonia. Usually, alkylammonium alkylcarbamates decompose into *symmetrical* dialkyl ureas (see p. 513). Thus:

$$RNH—CO_2NH_3R \longrightarrow RNH_2 + [RNH—CO_2H],$$

and

$$[RNH—CO_2H] \longrightarrow RNCO + H_2O \xrightarrow{RNH_2} (RNH)_2CO,$$

or

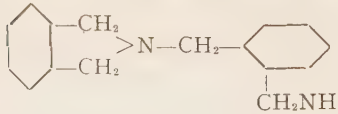
$$[RNH—CO_2H] \longrightarrow RNH_2 + CO_2.$$

However,[18] benzohydrylammonium benzohydrylcarbamate,

$$(C_6H_5)_2CHNHCO_2NH_3CH(C_6H_5)_2$$

gives none of the urea when heated in a sealed tube at 180-200°; nor does it yield benzohydrylamine. Instead, ammonia is evolved and tribenzohydrylamine is formed. Benzohydrylamine would appear to be a very reasonable intermediate product.

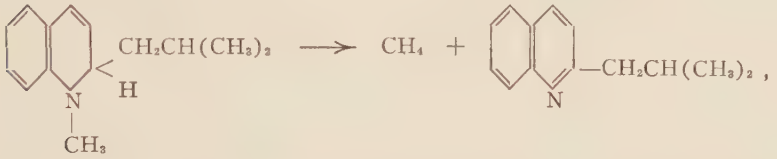
Triphenylmethyl-amine undergoes a pyrogenic decomposition[19] which is very much akin (p. 138) to that of triphenylmethyl bromide (or chloride). A sample of the amine, heated alone at 450°, gives a strong odor of ammonia and a residue of triphenylmethane, diphenylene-phenyl-methane, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CH—C_6H_5$, and resin.

Originally, it was thought that *o*-aminomethylbenzyl dihydroisoindole,  , possessed the 10 membered ring structure of "bisxylylenimine", $C_6H_4{=}(CH_2—NH—CH_2)_2{=}C_6H_4$. It is pointed out[20] that all such 10 and 11 membered rings are in error. On pyrolysis in a sealed tube, preferably in the presence of a little water, the substance yields two mols of dihydro*iso*indole, $C_6H_4\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>NH$.

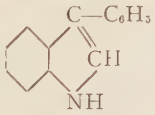
[17] Compare its formation from hydrobenzamide.
[18] Fichter and Becker, *Ber.* **44**, 3483 (1911).
[19] Stieglitz and Brown, *J. Am. Chem. Soc.* **44**, 1284 (1922).
[20] von Braun and Nelken, *Ber.* **55**, 2059 (1922); von Braun and Zobel, *Ann.* **445**, 247 (1925).

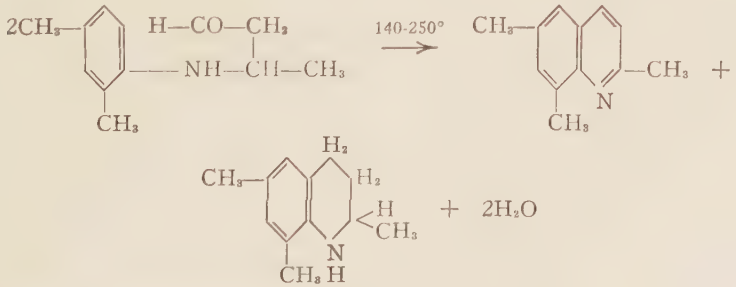
Similarly, ε-aminopentyl dihydro*iso*indole, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N-CH_2CH_2CH_2-CH_2CH_2NH_2$, undergoes decomposition into dihydro*iso*indole and piperidine. Such ketone amines as $RNH-CH_2COCH_3$, where R = H or alkyl, give water and indoles [21] when they are heated; the ketone amines are prepared from amines and chloro (or bromo)-acetone.

The following reaction:



proceeds by refluxing for 5 hours. From 17 grams of the original dihydroquinoline derivative there may be isolated 20 grams of the picrate of the final quinoline derivative.[22] The reaction proceeds fairly smoothly also with the analogous *N*-methyl-phenyldihydroquinoline (in the above equation, substitute phenyl for *iso*butyl). The yield in this case is 0.6 gram from 2 grams, and the temperature of the reaction is 250°.

When phenacyl-phenyl-amine, $C_6H_5COCH_2-NH-C_6H_5$, is dry-distilled,[23] at first some water and unchanged material passes over; finally, some 3-phenylindole,  , distils. The following reaction is of interest in a discussion [24] of the mechanism of Doebner and von Miller's quinaldine synthesis from aniline, acetaldehyde and concentrated hydrochloric acid:



[21] Richard, *Compt. rend.* **145**, 129 (1907).
[22] Meisenheimer, Stotz and Bauer, *Ber.* **58**, 2320 (1925).
[23] Möhlau, *Ber.* **18**, 165 (1885); **21**, 510 (1888).
[24] Jones and Evans, *J. Chem. Soc.* **99**, 334 (1911).

Pinenenitrolbenzylamine [25] undergoes the following transformation at 160-180°:

$$C_{10}H_{16}\begin{matrix}NO\\NH{-}CH_2C_6H_5\end{matrix} \longrightarrow (C_{10}H_{15}NO)_x + C_6H_5{-}CH_2NH_2.$$

An exactly analogous reaction from pinenenitrol*allyl*amine occurs at 160°. The residue which was isolated was a polymerization product of the simple nitroso-terpene.

Ammonium Hydroxides.

Except in the case of the quaternary hydroxides, there is nothing singular to record. From all others, the only effect of heat is to cause a separation of water and the base. In compounds of the quaternary type, however, this is no longer possible, and several interesting cases appear.

Quarternary Ammonium Hydroxides.

Tetramethylammonium hydroxide [26] decomposes on distillation into trimethyl amine and methanol:

$$(CH_3)_4NOH \longrightarrow (CH_3)_3N + CH_3OH$$

whereas the tetraethyl, or the tetrapropyl,[27] compounds do not give the corresponding alcohols, but instead yield the olefine and water. This is true even when aqueous solutions are distilled.

$$(C_2H_5)_4NOH \longrightarrow (C_2H_5)_3N + C_2H_4 + H_2O$$
$$(C_3H_7)_4NOH \longrightarrow (C_3H_7)_3N + C_3H_6 + H_2O.$$

When more than one alkyl group is present, it is obvious that there is a choice with reference to the radicals which remain attached to the nitrogen. Hofmann was the first to demonstrate that when the hydroxides of mixed quaternary ammonium compounds containing *ethyl* were heated, one of the ethyl groups was invariably eliminated in the form of ethylene. As shown by Collie and Schryver,[28] this becomes an excellent method for the synthesis of mixed tertiary amines. For example, in the distillation of methyl-amyl-diethyl-ammonium hydroxide, methyl-ethylamyl amine is produced.

In an effort to establish a quantitative basis regarding the relative ease of elimination of various radicals, von Braun [29] heated a number

[25] Wallach, *Ann.* **268**, 220 (1892).
[26] Hofmann, *Ber.* **14**, 494 (1881).
[27] Zander, *Ann.* **214**, 171 (1882).
[28] Collie and Schryver, *J. Chem. Soc.* **57**, 767 (1890).
[29] von Braun, *Ann.* **382**, 1 (1911).

of mixed quaternary ammonium hydroxides of the type $RN(CH_3)_3OH$, and determined the amount of methanol in each case. The following table indcates the nature of the radical R, and the percentage yield of methanol. In the second column are included similar results by Ingold.[30]

TABLE XXXIII.

R	(von Braun) Percent Methanol	(Ingold) Percent Methanol
heptyl, cetyl, octyl	75	..
(octyl); β-*n*-propyl-*n*-amyl	..	69
C_6H_5—$CH_2CH_2CH_2CH_2CH_2$—	75	..
hexyl	73	..
(hexyl); β-ethyl-*n*-butyl	..	57
amyl	60	..
CH_3O—$CH_2CH_2CH_2CH_2CH_2$—	60	..
H_2N—O—$(CH_2)_5$—	60	..
C_6H_5CONH—O—$(CH_2)_5$—	60	..
C_4H_5—O—$CH_2CH_2CH_2CH_2$—	55	..
n-butyl	50	25
*iso*butyl	..	37
n-propyl	5-10	19
tert. butyl	..	small
C_6H_5O—$CH_2CH_2CH_2$—	10	..
secondary amyl and *secondary* butyl	..	small
ethyl	negligible	zero
*iso*propyl	..	zero
phenylethyl	negligible	..
benzyl	negligible	..

This list may be supplemented [31] to include various alicyclic radicals. In this case, the estimation of the methanol content was based on the quantity of amines actually formed.

TABLE XXXIV.

R	Percent Methanol
cyclopropylmethyl, ▷—CH_2—	Over 90 percent; only 6.5 percent of hydrocarbons obtained, most of which is divinyl.
cyclopropyl, ▷—	40
cyclobutylmethyl, □—CH_2—	32
methylcyclopropylmethyl, ▷—$\overset{CH_3}{\overset{\vert}{C}}$H—	Very little if any.

The decomposition of methylcyclopropylmethyl-trimethyl-ammonium hydroxide gives trimethyl amine, and cyclopropyl-ethylene, $\begin{matrix}CH_2\\ \vert \\ CH_2\end{matrix}>CH—CH=CH_2$, in over 70 percent yields, and is by far the best

[30] Hanhart and Ingold, *J. Chem. Soc.* **1927**, 997.
[31] Demjanov and Dojarenko, *Ber.* **55**, 2718 (1922); **56**, 2200 (1923); *Bull. acad. sci. Russie* **16**, 297 (1922); *Chem. Abstracts* **20**, 2988 (1926).

way to prepare this olefine. The decomposition of cholines, which are also of the type, $RN(CH_3)_3OH$, shall be mentioned forthwith.

From these results, and others of a similar nature, it has been established that the phenyl radical is more firmly attached to the nitrogen than alkyl radicals, and that the allyl group is least firmly attached. A partial list of radicals indicating this relationship is, in fact, the electron attraction series (see p. 34).

> phenyl > cyclopropylmethyl > octyl > hexyl > *iso*amyl > methyl > butyl > *iso*butyl > cyclopropyl > propyl > ethyl > phenylethyl > *p*-nitrophenylethyl > benzyl > allyl.

As has been mentioned earlier (p. 38), the exact order of the intermediate radicals varies somewhat, depending on their method of determination.

The above series enables one to predict that in a compound such as phenylethyl-ethyl-dimethyl-ammonium hydroxide, more styrene than ethylene should result from heating:

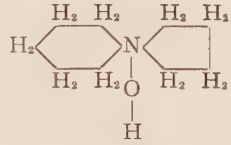
$$C_6H_5{-}CH_2{-}CH_2{-}\overset{\displaystyle C_2H_5}{\underset{|}{N}}(CH_3)_2OH \longrightarrow C_6H_5{-}CH{=}CH_2 + H_2O + \overset{\displaystyle C_2H_5}{\underset{|}{N}}(CH_3)_2$$

and such has been found to be the case.[30] Another illustration is ethylene and propyldimethyl amine, which are the major reaction products formed by distillation of an aqueous solution of dimethyl-ethyl-propyl-ammonium hydroxide. Only traces of methanol, propylene and methyl-ethylpropyl amine result. Since butyl and methyl do not differ markedly in their affinity capacities, it would be expected that both methanol and butylene should be formed in nearly equal quantities from butyl-trimethylammonium hydroxide. This is actually observed:

$$C_4H_9N(CH_3)_3OH \begin{cases} \nearrow C_4H_9{-}N(CH_3)_2 + CH_3OH \\ \searrow C_4H_8 + H_2O + N(CH_3)_3. \end{cases}$$

The formation of olefines instead of alcohols (thus, butylene + water, instead of butyl alcohol) was regarded by von Braun as evidence that the alcohol was not an intermediate product. This appears to be sound reasoning, from our knowledge of the behavior of alcohols at high temperatures. However, the methyl radical is not the only one to be eliminated as the alcohol inasmuch as from octyl- and cetyl-trimethylammonium hydroxides there is formed not only octylene but also octyl alcohol, and not only cetylene but also cetyl alcohol. Similarly, heptyl alcohol accompanies the formation of heptylene from heptyl-trimethylammonium hydroxide. The difficulty of producing carbon

chains with double linkages at the ends, therefore, increases as the chain becomes longer. Whether or not this is universally true needs more experimentation before it can be answered. In such compounds as $C_6H_5—O—(CH_2)_5—N(CH_3)_3OH$ or $C_6H_5—(CH_2)_5—N(CH_3)_3OH$, no reference was made to alcohol formation (other than methanol), but the unsaturated compound was mentioned.

Another case of "higher alcohol formation" appears [32] in the cyclic compound,  , which, on distillation, rearranges into 1-δ-hydroxybutyl-piperidine. The resistance offered to the disruption of the ring in such cases has been found to increase in the following order: dihydro*iso*indole and tetrahydro*iso*quinoline, pyrrolidine, piperidine and dihydroindole and tetrahydroquinoline. von Braun's experiments indicate that the loss of water in the Hofmann degradation may be an item of secondary consideration.

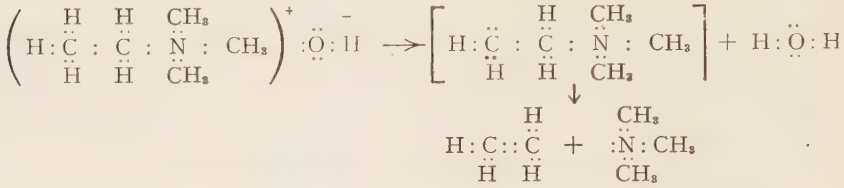
It is interesting to note [33] that tetraallyl-ammonium hydroxide changes by heating into *di*allylamine, almost exclusively. This unusual formation of a secondary amine instead of the tertiary triallylamine is in keeping with the fact that allyl is the group least firmly attached to nitrogen. Stewart and Aston [34] have reported another instance wherein a quaternary ammonium hydroxide changes into a secondary amine. Ethoxymethyl-methyl-diethylammonium hydroxide gives ethylene and 81.5 mol-percent of methylethyl amine by evaporation at room temperature and 0.05 mm.:

$$(C_2H_5)_2\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{N}}—CH_2—O—C_2H_5 \longrightarrow C_2H_5—NH—CH_3 + C_2H_4 + CH_2O + C_2H_5OH$$

A side reaction gives rise to 18 percent of methyldiethyl amine, but this becomes the major reaction (90 percent yield) if the hydroxide is distilled at 140-150°.

To explain the mechanism of the decomposition of quaternary ammonium hydroxides, Hanhart and Ingold have assumed an incipient ionization for a hydrogen on a β-carbon atom; it is then considered to leave its valence electrons to attach itself to the hydroxyl group, thereby forming water.

[32] von Braun, *Ber.* **49**, 2629 (1916).
[33] Solonina, *J. Russ. Phys. Chem. Soc.* **38**, 1286 (1907); *Chem. Abstracts* **1**, 2086 (1907).
[34] Stewart and Aston, *J. Am. Chem. Soc.* **49**, 1718 (1927).



In the readjustment process, ethylene and triphenylamine are formed. Groups which are attached to the β-carbon are considered to exert more influence on the decomposition than groups on the α-carbon.

A few individual cases will be cited. It has already been mentioned that cyclopropyl ethylene is best formed by heating the quaternary compound. Demjanov and Dojarenko (Reference 31) have also shown that a 60 percent yield of cyclopropene, $\begin{matrix}CH{=}CH\\ \diagdown\!\diagup\\ CH_2\end{matrix}$, may be formed by heating cyclopropyl-trimethyl-ammonium hydroxide. The isomeric compound, methyl acetylene, is also produced in small amounts but this may be readily removed by ammoniacal cuprous chloride. To a smaller extent, there is a breakdown into methanol and cyclopropyl-dimethylamine. Parenthetically, it may be remarked that cyclopropene was originally discovered as a dry distillation product of barium furoate (see p. 493).

von Braun[35] has obtained interesting results with quaternary hydroxides of the type, $(CH_3)_3N{-}(CH_2)_x{-}N(CH_3)_3$, where x = 3, 5, 7 and 10. Three general reactions may be considered, all of which were encountered.

(1) Decomposition into $(CH_3)_2N{-}(CH_2)_x{-}N(CH_3)_2 + 2CH_3OH$. This reaction is negligible when $x = 3$ or 5, but 50 percent amounts are realized when $x = 7$ or 10; that is, in the heptane and decane series.

(2) Decomposition into $CH_2{=}CH{-}(CH_2)_{x-2}{-}N(CH_3)_2 + (CH_3)_3N + H_2O + CH_3OH$. All four types give this reaction, but in very small yields when $x = 3$ or 5; when $x = 7$ or 10, the yields according to this reaction are about 30 percent.

(3) Decomposition into $C_xH_{2x-2} + 2(CH_3)_3N + 2H_2O$. When $x = 10$, this reaction is realized to less than 20 percent; when $x = 7$, the yield of heptadiene is about 15 percent; when $x = 5$, the decomposition into piperylene is almost the exclusive reaction. A peculiar situation arises when $x = 3$, for the diene which the equation would suggest is allene, $CH_2{=}C{=}CH_2$. Allene, however, is not formed, but the residue, $\left[\begin{matrix}CH_2{-}C{-}CH_2\\ \diagdown\!\diagup\end{matrix}\right]$, which may be considered to be formed momentarily, reacts with the water to produce a ketone, $C_6H_{10}O$, which is actually isolated. A possible formula which was suggested for this ketone is

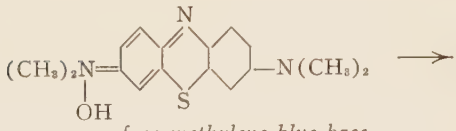
$$CH_3COCH_2{-}C(CH_3){=}CH_2.$$

[35] von Braun, *Ann.* 386, 273 (1912).

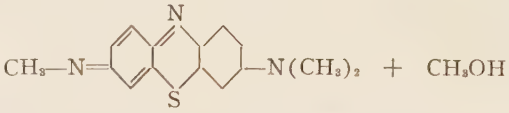
The reaction of decomposition, when $x = 4$, has been made the subject of a patent.[36] Butadiene is formed:

$$(CH_3)_3N{-}CH_2CH_2CH_2CH_2{-}N(CH_3)_3 \longrightarrow 2(CH_3)_3N + 2H_2O + C_4H_6$$
$$\quad\quad\quad

It is also interesting to record the following case:[39]



free methylene blue base



trimethyl thionin

(β-Diethylaminoethyl)-trimethylammonium hydroxide[40] breaks down chiefly as follows:

$$(C_2H_5)_2N{-}CH_2CH_2{-}N(CH_3)_3OH \longrightarrow (C_2H_5)_2N{-}CH_2CH_2{-}N(CH_3)_2 + CH_3OH.$$

Nevertheless, a small portion also changes into trimethylamine, water and diethyl-vinyl-amine. Neurine, $(CH_3)_3N{<}^{CH=CH_2}_{OH}$, changes largely into trimethylamine and acetaldehyde (vinyl alcohol), but a small portion becomes transformed into methanol and dimethyl-vinyl-amine.

Cholines.

Both of the possible modes of decomposition occur in the dry distillation of choline, but the reaction into trimethylamine and glycol predominates:

$$(CH_3)_3N{<}^{CH_2CH_2OH}_{OH} \rightleftarrows \begin{cases} (CH_3)_3N + CH_2OH{-}CH_2OH \\ (CH_3)_2N{-}CH_2CH_2OH + CH_3OH \end{cases}$$

From 20 grams of choline, there may be formed 5 cc. of glycol and 2 cc. of β-hydroxyethyl-dimethyl-amine. Evidence that the latter substance becomes partially dehydrated is furnished by the isolation of 0.1 gram of dimethylvinylamine, $(CH_3)_2N{-}CH{=}CH_2$.

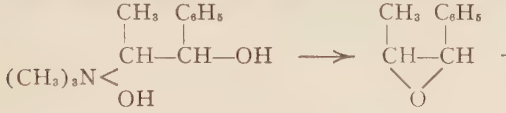
From phenylalanine choline,[41] the decomposition leading to trimethylamine appears to be the exclusive one. In this case:

$$(CH_3)_3N{<}^{CH_2{-}C_6H_5}_{CH{-}CH_2OH} \longrightarrow {}^{CH{-}C_6H_5}_{\|}{}_{CH{-}CH_2OH} + (CH_3)_3N + H_2O,$$

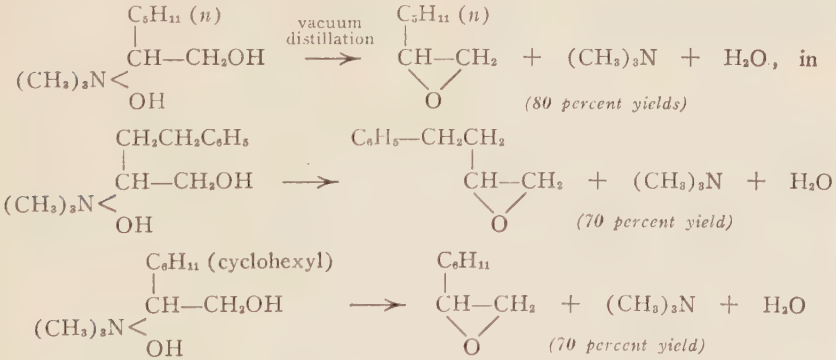
[39] Bernthsen, *Ann.* **230**, 145 (1885).
[40] K. Meyer and Hopff, *Ber.* **54**, 2274 (1921).
[41] Karrer and Horlacher, *Helv. Chim. Acta* **5**, 571 (1922).

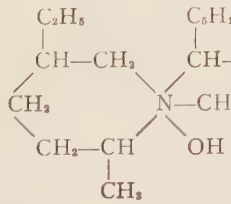
and it will be noticed that the glycol does not form, and that the hydrogen on the β-carbon atom (not holding the hydroxyl group) is the one which unites with the hydroxyl to form water. If the phenyl group in this reaction is replaced by *p*-anisyl, the reaction proceeds smoothly to yield anisyl allyl alcohol.

Still another method of decomposition is the well-known reaction for other substituted cholines, which leads to the formation of an ethylene oxide derivative, frequently in excellent yields.[42] To illustrate:



Comparison of this choline with the one which was mentioned in the preceding equation shows that they are both isomeric, and that in both cases the phenyl group is attached to a β-carbon atom. In the latter case, the phenyl and the hydroxyl are attached to the same hydroxyl, but apparently this is not essential, as the following cases reveal. In the above illustration, some of the glycol is also formed, but in the cases to follow [43] none is produced. These will be given without comment:



In the case of  one-third of the decomposition leads to methanol and the amine, $C_8H_{16}{=}N{-}\overset{C_5H_{11}}{\overset{|}{C}}H{-}CH_2OH$. The

[42] Rabe and Hallensleben, *Ber.* **43**, 2622 (1910).
[43] von Braun and Schirmacher, *Ber.* **56**, 1845 (1923); von Braun, *ibid.* p. 2178.

major reaction, however, leads to pentyl ethylene oxide, $C_5H_{11}—CH—CH_2$ (O), water, and the amine, $C_8H_{16}=N—CH_3$.

The choline [44] from β-dimethylamino-ε-phenylpentyl alcohol, $C_6H_5CH_2CH_2C(N(CH_3)_3OH)—CH_2—CH_2OH$, if heated under diminished pressure, yields 40 percent of γ-phenylpropyl-ethylene oxide, about 30 percent of what appears to be a polymer of this substance, and about 10 percent of the related glycol. The choline from β-dimethylamino-β-cyclopentyl alcohol, $C_5H_9—CH(N(CH_3)_3OH)—CH_2OH$, also gives some of the expected cyclopentyl-ethylene oxide, but the yields are small. From this, it seems that the 5-membered cyclopentyl radical is much less efficient for this reaction than the 6-membered cyclohexyl radical. Some of the glycol also accompanies the formation of cyclopentyl-ethylene oxide, but its yield is small also.

2,8-Dipiperidino-nonandiol-1,9, $CH_2(CH_2CH_2CH(N=C_5H_{10})—CH_2OH)_2$, which is prepared from diethyl α,α'-dibromoazelaate, may be converted to the methiodide and treated with silver oxide and distilled. Some methyl-piperidine and a small amount of substance thought to be the bis-oxide, $CH_2(CH_2CH_2—CH(O)—CH_2)_2$, are formed. 2,5-Dipiperidino-hexandiol-1,6 may be subjected to a similar series of reactions, with much the same results.

Finally, the decomposition [45] of a "choline methyl ether", which has no available hydrogens on the β-carbon atom, is of unusual interest since it involves the migration of a methoxyl group:

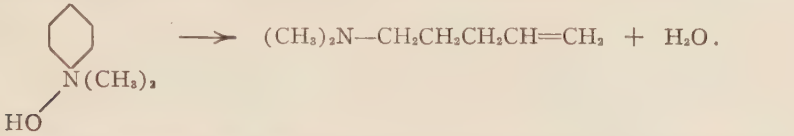
$$(CH_3)_3N<\begin{matrix}CH_2—C(CH_3)—OCH_3\\ OH\quad C_6H_5\end{matrix} \longrightarrow (CH_3)_3N + H_2O + CH_3O—CH=C(C_6H_5)—CH_3.$$

Cyclic Quaternary Ammonium Hydroxides.

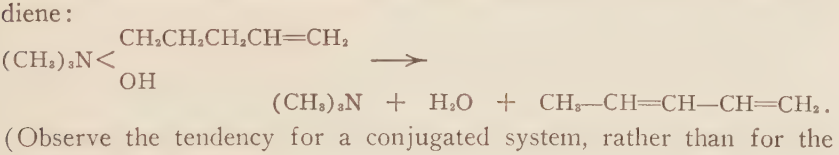
The pyrolysis of the quaternary ammonium hydroxide related to *N*-methyl-granatenine has already been given, as have some quaternary compounds related to piperidine. There are many more such cases. The formation of tertiary, unsaturated amines through the ring-splitting of a quaternary cyclic base was discovered [46] by A. W. Hofmann, and this

[44] von Braun and Münch, *Ber.* **59**, 1941 (1926).
[45] Tiffeneau, *Compt. rend.* **158**, 1580 (1914).
[46] Hofmann, *Ber.* **14**, 661 (1881).

reaction is named after him. Thus, in the distillation of dimethylpiperidinium hydroxide, there is formed dimethylamino-pentene:

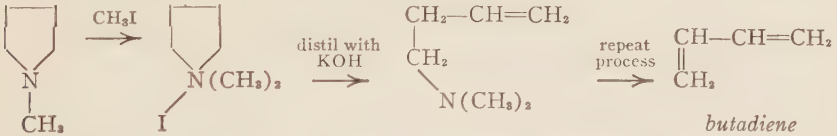


This type of reaction has been studied [47] by Ladenburg, and by Merling and in recent years particularly by von Braun. The tertiary amine which is the product of the reaction may, of course, be converted into another quaternary ammonium base, distillation of which produces a diene:

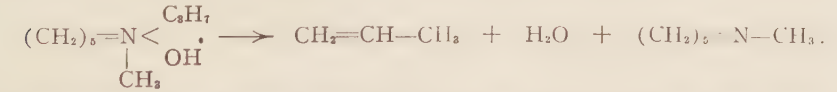


(Observe the tendency for a conjugated system, rather than for the production of pentadiene-1,4.)

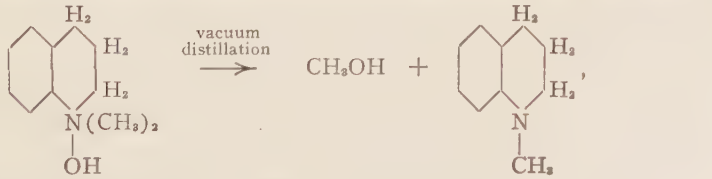
The same type of decomposition may be induced with methylpyrrolidine as the beginning material:



It could be anticipated that groups other than methyl might easily cause the formation of a different olefine and a different tertiary amine. This, in fact, actually is what happens. Whereas dimethylpiperidinium hydroxide becomes transformed into dimethylamino-pentene, the *N*-propyl analog [48] yields propylene and methyl piperidine:

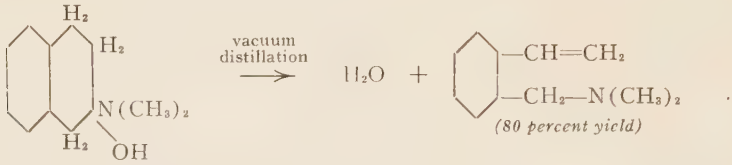


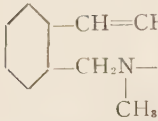
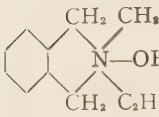
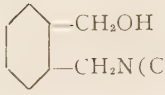
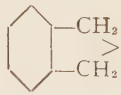
Furthermore, the bases formed from tetrahydroquinoline and tetrahydro*iso*quinoline do not behave in a parallel manner. In the first case,[49]



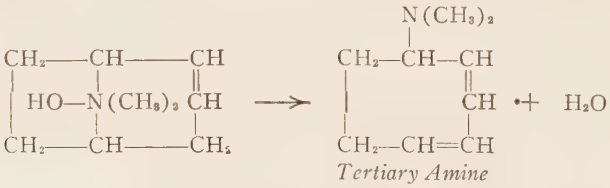
[47] Ladenburg, *Ber.* **16**, 2058 (1883); Merling, *Ber.* **17**, 2139 (1884); **19**, 2628 (1886); *Ann.* **264**, 310 (1891).
[48] von Braun, *Ber.* **42**, 2532 (1909).
[49] Möller, *Ann.* **242**, 320 (1887).

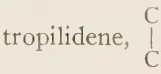
whereas in the latter,[50]



The homologous *N*-ethyl compound behaves similarly and gives  . The corresponding base from dihydro*iso*indole,  , does give some of the *o*-hydroxymethyl compound,  , by severing the carbon-to-nitrogen bond, but the chief reaction is an elimination of ethylene, giving  . *N*-methyl-dihydro*iso*indole.

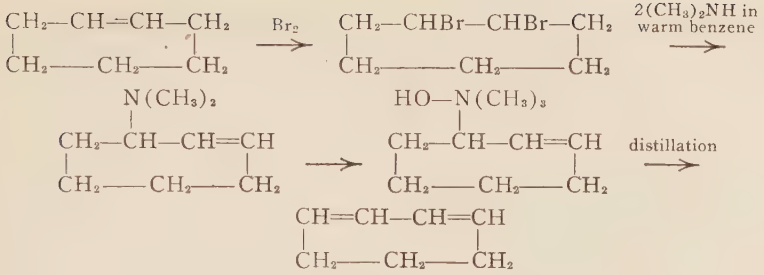
In addition to the transformation of *N*-methyl-granatenine (p. 303) into cyclooctatriene, Willstätter [51] has also recorded other experiments in bicyclic systems. The steps for some of these transformations will be briefly indicated. Observe that in all cases, conjugate double bonds are formed.



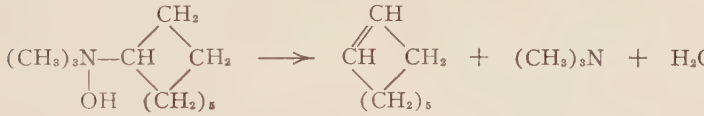
The new tertiary amine may be easily converted into the quaternary ammonium hydroxide, $C_7H_9—N(CH_3)_3—OH$, which by distillation then yields tropilidene,  . Also, the preparation of cycloheptadiene in 26.7 grams yield from cycloheptene (49.8 grams) through the following four steps:

[50] Emde, *Ann.* **391**, 100 (1912); von Braun, *Ber.* **50**, 45 (1917); von Braun and Köhler, *Ber.* **51**, 100 (1918).

[51] Willstätter, *Ann.* **317**, 272 (1901); Willstätter and Waser, *Ber.* **43**, 1180 (1910); Willstätter, *Ber.* **34**, 129 (1901).

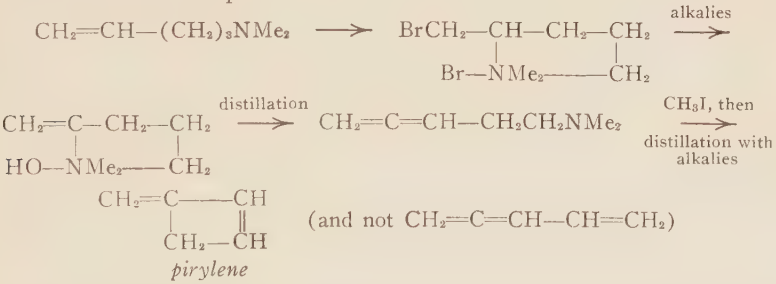


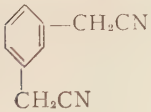
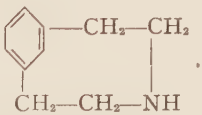
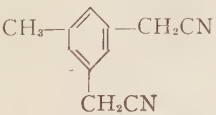
The synthesis of cyclooctene follows an analogous course:



by distillation at ordinary pressure.

The synthesis of pirylene [51a] is of interest. The following sequence shows the essential steps:



Quite recently, von Braun claimed to have effected a ring closure [52] through the *meta* position by reducing phenylene-acetonitrile,  . An amine was formed, and he considered the most probable formula to be  . A homologous amine of very similar nature was likewise obtained from 5-methyl-phenyleneaceto-nitrile,  . Such *meta* ring closures involve so startling

[51a] von Braun and Teuffert, *Ber.* **61**, 1092 (1928).
[52] von Braun, Karpf and Garn, *Ber.* **53**, 98 (1920); von Braun and Engel, *Ber.* **58**, 281 (1925).

a departure from the orthodox reactions of organic chemistry that they would be of great theoretical value if they could be substantiated. However, Titley [53] has demonstrated that the amine is not a bicyclic compound, but is *β-m*-tolylethylamine, CH_3— —CH_2—CH_2—NH_2.

The course of the Hofmann degradation, as described by von Braun with his supposed bicyclic secondary amine, must, therefore, receive an interpretation on this basis. By exhaustive methylation and heating of the quaternary ammonium hydroxide, CH_3— —CH_2—CH_2—$N(CH_3)_3OH$, one would predict a decomposition into trimethylamine, water, and *m*-methyl-styrene, CH_3— —$CH{=}CH_2$. In contradiction to some of von Braun's evidence, Titley has proved that this is exactly what happens. A footnote in Titley's paper, by Perkin, indicates that von Braun accepts Titley's evidence.

Substituted Ammonium Salts of Inorganic Acids.

Because of the intimate relationship of the decomposition of the ammonium hydroxides and of their salts, the pyrolysis of the ammonium salts of inorganic acids will be sketched at this time. Other ammonium salts will be treated in a later chapter.

Substituted Ammonium Halides. We are so accustomed to think of the pyrolytic dissociation of ammonium chloride into $NH_3 + HCl$, that it would be surprising if the alkylammonium chlorides were not placed in the same category. As will be seen, however, this is usually a minor reaction, if it occurs at all. *Ethylammonium chloride* has been found to pyrolyze (270°) into ethyl and diethyl amines, ammonia, ethylene and ethyl chloride. This seems to indicate the two concurrent reactions:

$$CH_3CH_2NH_3Cl \longrightarrow CH_2{=}CH_2 + NH_4Cl \quad (NH_3 + HCl)$$
$$CH_3CH_2NH_3Cl \longrightarrow CH_3CH_2NH_2 + HCl,$$

and a secondary reaction between ethylammonium chloride and ethyl amine to produce diethylamine and ammonium chloride.[54]

Trimethylammonium chloride, at 280°, is reported [55] to decompose into trimethylamine, methyl chloride and methylammonium chloride; at 300°, ammonia appears, and at 325° the pyrolysis into ammonia and methyl chloride is so complete that, in the presence of more hydrogen

[53] Titley, *J. Chem. Soc.* **1926**, 508.
[54] Fileti and Piccini, *Ber.* **12**, 1508 (1879).
[55] Vincent, *Compt. rend.* **84**, 1139 (1877); **85**, 667 (1877).

chloride, this becomes a very satisfactory method of preparing methyl chloride. The trimethylammonium chloride is a by-product of beet sugar manufacture.

$$(CH_3)_3NHCl + 3HCl \longrightarrow 3CH_3Cl + NH_4Cl.$$

Quite analogously, the hydrochloride of dimethylaniline [56] becomes transformed into methyl chloride and aniline hydrochloride (free from toluidine), by heating at 180° in the presence of hydrogen chloride:

$$C_6H_5—NH(CH_3)_2—Cl + 2HCl \longrightarrow 2CH_3Cl + C_6H_5NH_3Cl.$$

Trimethylammonium bromide decomposes at 300°, and the products of decomposition are methyl bromide, ammonia, trimethylamine and tetramethylammonium bromide. The iodide begins to pyrolyze at 210° and at 280° the gaseous evolution is vigorous. Methyl iodide, ammonia, trimethylamine, and tetramethylammonium iodide are produced.

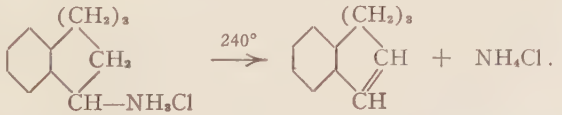
It will be noticed in the next few reactions, that almost the exclusive reaction is the one leading to the formation of an unsaturated compound as ammonium chloride is eliminated:

$$—CH(NH_3Cl)—CH_2— \longrightarrow —CH=CH— + NH_4Cl.$$

The final step of one of the most suitable synthetic methods for the preparation of indene [57] is to heat the hydrochloride of 1-aminohydrindene at 250°:

95 percent yield

The complete synthesis starts with cinnamic acid, and proceeds by steps through hydrocinnamic acid, hydrocinnamyl chloride, α-hydrindone and its oxime, and by reduction of the latter to 1-aminohydrindene. The preparation of phencycloheptene [58] follows a similar course:



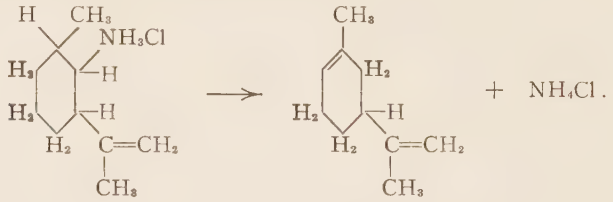
[56] Lauth, *Ber.* **6**, 677 (1873).
[57] Kipping and Hall, *J. Chem. Soc.* **77**, 468 (1900).
[58] Kipping and Hunter, *ibid.* **83**, 246 (1903).

Cymene may be formed by distilling pinylamine hydrochloride (melting point 230°, with decomposition), and other terpene derivatives [59] behave similarly.

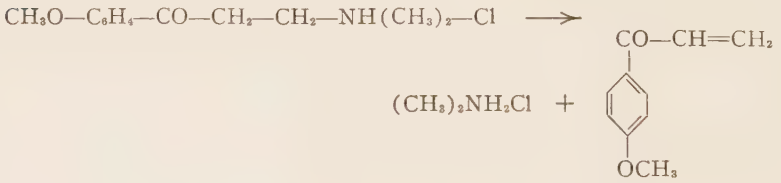
$$C_{10}H_{15}NH_3Cl \longrightarrow NH_4Cl + (CH_3)_2CH{-}C_6H_4{-}CH_3.$$

A considerable quantity of cymene [60] also is produced when dihydrocarvylamine hydrochloride is heated above its melting point, 184°, but the chief product is terpinene:

The transformation [61] of vestrylamine hydrochloride into carvestrene, by dry-distilling in a current of hydrogen chloride, is very similar:



Another illustration, which is not related to terpenes, follows.[62] The reaction takes place at a temperature of 180° and 20 mm. pressure.



These cases provide a satisfactory basis for the interpretation of results from the distillation [63] of the hydrochloride of either ephedrine or of its stereoisomer, pseudo-ephedrine. In a carbon dioxide atmosphere the products are propiophenone and methyl amine at 230-240°, and if the pyrolysis is conducted at 250-260° some ammonium chloride

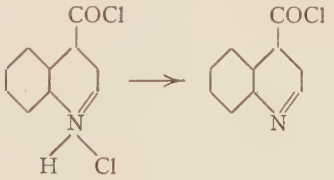
[59] Wallach, *Ann.* **268**, 206 (1892)
[60] Wallach, *Ber.* **24**, 3986 (1891); *Ann.* **275**, 125 (1893).
[61] Baeyer, *Ber.* **27**, 3488 (1894).
[62] Mannich and Lammering, *Ber.* **55**, 3510 (1922)
[63] Schmidt, *Arch. Pharm.* **252**, 89 (1914).

and trimethylamine are also formed. In conformity with other illustrations, the steps may be represented through an intermediate enol:

$$CH_3—\underset{\displaystyle Cl—NH_2—CH_3}{\overset{|}{CH}}—CHOH—C_6H_5 \longrightarrow CH_3NH_3Cl +$$

$$[CH_3—CH{=}C(OH)—C_6H_5] \longrightarrow CH_3—CH_2—CO—C_6H_5.$$

On heating, the hydrochloride of pyridine dissociates into pyridine. A similar case of recent interest [64] is the dissociation of cinchonyl chloride hydrochloride into cinchonyl chloride by distilling it in a vacuum:



Substituted Ammonium Nitrites. In much the manner that ammonium nitrite pyrolyzes into water and nitrogen, so the alkylammonium nitrites change into alcohol, water and nitrogen:

$$R—NH_3—O—NO \longrightarrow ROH + H_2O + N_2.$$

This is a characteristic behavior which is realized merely by the interaction of a solution of nitrous acid with a primary amine. Presumably, the intermediate step is the formation of a nitroso (or *iso*nitroso) derivative, RNH—NO (or R—N=NOH), but this is too unstable to isolate. We are accustomed to regard this decomposition as spontaneous, but with nitrites prepared in the absence of water, many of them show a surprising stability. Noyes [65] found this to be true with the nitrite from 3-aminopentane, $(C_2H_5)_2CH—NH_3—ONO$, and he reported that the solution of the nitrite from 4-aminoheptane must be boiled 45 minutes for 80 percent of the nitrogen to be evolved. Benzohydrylammonium nitrite, $(C_6H_5)_2CHNH_3—ONO$, in concentrated aqueous solution, loses 83 percent of its nitrogen in half an hour at 100°, forming benzohydrol.

The primary, secondary and tertiary ammonium nitrites [66] exhibit the order of stability which would be expected from the heat of neutralization of the corresponding amines with hydrochloric acid. In round numbers, methyl and ethyl amine evolve 26,000 calories; dimethylamine, 23,000 calories; and trimethylamine, 17,000 calories. Trimethylammonium nitrite is the least stable, and methylammonium nitrite

[64] Spath and Spitzer, *Ber.* **59**, 1477 (1926).
[65] Noyes, *Am. Chem. J.* **15**, 539 (1893), Noyes and Ballard, *ibid.* **16**, 449 (1894).
[66] Ray and Rakshit, *J. Chem. Soc.* **99**, 1470 (1911).

(primary) the most. All of these compounds display a tendency to dissociate, but trimethylammonium nitrite (dry) completely dissociates at 100° when heated in the vacuum of a mercury pump into nitrous acid (or its decomposition products) and trimethylamine. The equation for this change appears to be the following:

$$3(CH_3)_3NHONO \longrightarrow (CH_3)_3NHONO_2 + 2NO + H_2O + 2(CH_3)_3N.$$

Ethylammonium nitrite breaks down at 60°, *in vacuo,* into water and alcohol, but the distillate responds to the nitroso test, indicative of diethyl-nitrosamine:

$$2C_2H_5NH_3ONO \longrightarrow N_2 + 3H_2O + (C_2H_5)_2N{-}NO.$$

Nitrogen, nitric oxide and traces of ethylamine are in the gas. Many years ago, Linnemann [67] observed a similar fact, namely, the formation of dipropyl-nitrosamine, in addition to propyl alcohol, when an aqueous solution of propylammonium nitrite is heated. Furthermore, he recognized the fact that the alcohol was not *n*-propyl, but *iso*propyl-alcohol. Also, Linnemann noticed that *iso*butyl alcohol, and not *n*-butyl alcohol, results from the decomposition of butylammonium nitrite. These same phenomena [68] were noticed by Ray and Rakshit. Both *n*-propyl- and *n*-butyl-ammonium nitrite decompose slowly at 32° in a high vacuum, and at 70-75° the pyrolysis is fairly rapid. The former appears to undergo a 3-directional decomposition:

$$C_3H_7NH_3ONO \longrightarrow \textit{iso}\text{-}C_3H_7OH + N_2 + H_2O$$
$$2C_3H_7NH_3ONO \longrightarrow (C_3H_7)_2N{-}NO + N_2 + 3H_2O$$
$$3C_3H_7NH_3ONO \longrightarrow C_3H_7NH_3ONO_2 + 2NO + C_3H_7NH_2 + H_2O.$$

Butylammonium nitrite gives *iso*butyl alcohol, as stated; it also gives the nitroso compound, and pure nitrogen as the gas. A reasonable explanation might be given for the appearance of *iso*propyl alcohol, from the *n*-propyl salt, but none seems apparent to account for the isomerization of *n*-butyl into *iso*butyl. The latter involves a shortening of the carbon chain; however, the secondary butyl group would not be open to this objection, but it was not mentioned.

Benzylammonium nitrite [69] sublimes at 85° in a high vacuum, but above 85° decomposition sets in with the formation of benzyl alcohol, water and nitrogen (no nitric oxide).

Hellerman [70] has obtained some interesting results with β,β,β-triphenylethyl-ammonium nitrite. At its melting point, 138°, nitrogen is evolved, but without the formation of even traces of triphenyl-ethanol.

[67] Linnemann, *Ann.* **161**, 47 (1872); **162**, 5 (1872).
[68] Ray and Rakshit, *J. Chem. Soc.* **101**, 141 (1912).
[69] Ray and Datta, *J. Chem. Soc.* **99**, 1475 (1911).
[70] Hellerman, Cohn and Hoen, *J. Am. Chem. Soc.* **50**, 1716 (1928).

Instead, the products are triphenyl-ethylene (55 percent); β,β,β-triphenylethyl-ammonium nitrate (10 percent); and β,β,β-triphenylethyl amine for the remainder. Thus:

$$(C_6H_5)_3C{-}CH_2{-}NH_3{-}ONO \rightarrow \begin{cases} (C_6H_5)_2C{=}CH{-}C_6H_5 \\ (C_6H_5)_3C{-}CH_2NH_2 \\ (C_6H_5)_3C{-}CH_2{-}NH_3{-}ONO_2. \end{cases}$$

The formation of the amine is, of course, readily enough explained by dissociation of the nitrite into the amine and nitrous acid, the latter becoming partially converted into nitric acid. This explains the 10 percent of nitrate also. The mechanism for explaining the 55 percent of triphenyl ethylene is certainly less apparent, but it seems that there are but two reasonable choices. One is to assume an ephemeral existence of triphenylmethyl carbinol, which on rearranging into diphenyl benzyl carbinol would become simultaneously dehydrated to the olefine. The other is to assume the momentary presence of triphenyl methylene, $(C_6H_5)_3C{-}CH{=}$, which would then rearrange into triphenyl ethylene. Hellerman prefers the latter mechanism, and he has produced some interesting evidence in its favor. If this pyrolysis is performed in the presence of mercuric oxide, triphenylacetaldehyde [71] results, a reaction which is very neatly explained through triphenylmethyl methylene:

$$(C_6H_5)_3C{-}CH{=} + HgO \longrightarrow (C_6H_5)_3C{-}CH{=}O + Hg.$$

Usually, dialkylammonium nitrites change into the nitroso compound when they are heated:

$$R_2NH_2{-}O{-}NO \longrightarrow R_2N{-}NO + H_2O.$$

Such is the case, for example, with dimethylammonium nitrite.[66] The pure salt decomposes at 60° in a high vacuum. In addition to the nitroso compound, small amounts of methanol are also formed as the result of a secondary reaction:

$$(CH_3)_2NH_2ONO \longrightarrow N_2 + 2CH_3OH.$$

Nitrogen, and a trace of dimethylamine, appear as gaseous products, and a slight residue of dimethylammonium nitr*ate* remains. Under the vacuum of the mercury pump, the greater portion of *dibenzylammonium nitrite* sublimes without change, but there is also some decomposition into dibenzylamine, dibenzyl-ammonium nitrate, and nitric oxide. This is again an indication of dissociation, followed [72] by simultaneous oxidation and reduction of the nitrous acid:

$$3(C_7H_7)_2NH_2ONO \longrightarrow (C_7H_7)_2NH_2ONO_2 + 2NO + H_2O + 2(C_7H_7)_2NH.$$

[71] Two different triphenylacetaldehydes are extant in the literature; this one melts at 105°.
[72] Ray and Datta, *J. Chem. Soc.* **99**, 1475 (1911).

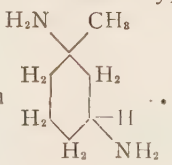
At 110-120°, *piperidinium nitrite*, $(CH_2)_5{=}NH_2ONO$, becomes dehydrated [73] to nitrosopiperidine.

As expounded earlier, the nitrites of most tertiary amines are dissociated into nitrous acid and the amine, but in some cases [33] they are decomposed into the nitroso derivatives of secondary amines. The yield of the nitroso compound is greater the stronger the amine. In mixed amines containing both propyl groups, the *n*-propyl group shows the greater tendency to be eliminated. For example, *n*-propyl is more readily replaced by nitroso than *iso*propyl. The nitrite of di-*n*-propyl-*iso*propyl-amine changes exclusively into the nitroso derivative of *iso*propyl-*n*-propyl-amine, whereas di-*iso*propyl-*n*-propyl-amine yields a mixture of di-*iso*propyl nitrosamine and *iso*propyl-*n*-propyl nitrosamine.

Other Substituted Salts. Dimethylammonium nitrate (not nitrite) undergoes [74] an exothermal decomposition at 150°; dimethyl nitrosamine distils in 53-54 percent yields. Other products of the reaction are nitrogen, carbon dioxide and formic acid. Good yields of diethyl nitrosamine are obtainable in a similar manner (at 170°) from diethylammonium nitrate. The temperature for the pyrolysis of tetraethylammonium nitrate is 230°. The reported products of the reaction are carbon, triethylamine and gases.

Distillation [75] of the *phosphate* of 1,3-diamino-cyclohexane gives 1,3-cyclohexadiene. Ammonia and ammonium pyrophosphate are also produced. This reaction, as well as the previous ones in which ammonium chloride was eliminated, undoubtedly succeeds because of the inert nature of the salt which is formed. The *sulfates* of the amines give significant amounts of sulfides in their thermal decompositions according to Harries.

Harries obtained a 60 percent yield of methyl isoprene, $CH_2{=}C(CH_3){-}CH{=}CH{-}CH_3$, when the phosphate of $(CH_3)_2C(NH_2){-}CH_2{-}CH(NH_2){-}CH_3$ was dry-distilled. As before, ammonia was also evolved and ammonium pyrophosphate was the residue. Similarly, a dihydrotoluene (5,6 or 2,5 or 4,5) was formed from



[73] Neogi, *ibid.* **99**, 1598 (1911).
[74] Romburgh, *Rec. trav. chim.* **5**, 246 (1886).
[75] Harries and Antoni, *Meyer and Jacobson*, "Lehrbuch," II, 1, 797; Harries, *Ber.* **34**, 300 (1901).

Quaternary Ammonium Salts.

One very noteworthy difference between the mode of decomposition of quaternary ammonium salts (chlorides) and quaternary ammonium hydroxides is that the former usually pyrolyze into tertiary amines and alkyl halides:

$$R_3N{<}^{R'}_{X} \longrightarrow R_3N + R'X,$$

whereas the hydroxides usually give olefines. It is found, furthermore, that the order of the firmness of attachment of the radical R′ is not identical in the two cases. With quaternary ammonium salts, this order is: phenyl > amyl > butyl > propyl > ethyl > methyl > benzyl > allyl. As compared with the series for the hydroxides (p. 300), it will be seen [76] that *methyl* follows *ethyl* instead of following *amyl;* otherwise, the list is similar.

Tetramethylammonium fluoride undergoes pyrolysis at 180° in a vacuum, and the chloride breaks down at 360°. In each case, [77] trimethylamine and methyl halide are formed. The iodide [78] decomposes similarly at 150°:

$$(CH_3)_4NI \longrightarrow CH_3I + (CH_3)_3N.$$

Batuecas [79] has prepared methyl chloride of especial purity, for the determination of the atomic weight of chlorine, from tetramethylammonium chloride, by pyrolysis.

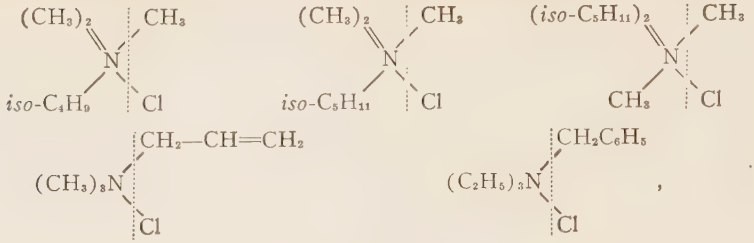
In accord with the series given above, methyl-triethylammonium chloride undergoes decomposition [80] chiefly into methyl chloride and triethylamine:

$$(C_2H_5)_3NCl{-}CH_3 \longrightarrow CH_3Cl + (C_2H_5)_3N,$$

and with ethyl-trimethylammonium chloride into methyl chloride and dimethyl-ethyl-amine. In these reactions, a small amount of ethyl chloride and trimethylamine is also produced, but this might be anticipated. Dimethyldiethylammonium chloride pyrolyzes [81] not only into methyl chloride and methyl-diethyl-amine, but also into a smaller amount of ethyl chloride and ethyl-dimethyl-amine.

Other cases described by Collie and Schryver in which R′X was eliminated from $R_3R'NX$ in accord with the above series were:

[76] von Braun, *Ann.* **382**, 1 (1911); von Meyer, *Chem. Abstracts* **5**, 887 (1911).
[77] Lawson and Collie, *J. Chem. Soc.* **53**, 627 (1888).
[78] Staudinger and Meyer, *Helv. Chim. Acta* **2**, 608 (1919).
[79] Batuecas, *Anales soc. espaň. fis. quim.* **24**, 528 (1926).
[80] Collie and Schryver, *J. Chem. Soc.* **57**, 768 (1890).
[81] Meyer and Lecco, *Ann.* **180**, 177 (1875); Lossen, *Ann.* **181**, 380 (1876).



but in the following cases the decompositions were at variance:

$$(CH_3)_3N{<}\begin{matrix}C_3H_7(n\text{- or }iso\text{-})\\Cl\end{matrix} \longrightarrow (CH_3)_3N + C_3H_7Cl \quad (chiefly)$$

$$(CH_3)_3N{<}\begin{matrix}C_5H_{11}(n)\\Cl\end{matrix} \longrightarrow (CH_3)_3N + C_5H_{11}Cl \quad (chiefly)$$

It is found [82] also that when *iso*propyl iodide and triethylamine are allowed to react at 100°, instead of an addition product, propylene and triethylammonium iodide are formed. Similarly, with triethylamine and tertiary butyl bromide, the product is *iso*butylene, and in like manner, triethylamine changes either of the two methylbromoethylenes into methyl acetylene. Curiously, however, allyl bromide yields

$$(C_2H_5)_3N{<}\begin{matrix}CH_2{-}CH{=}CH_2\\Br\end{matrix}.$$

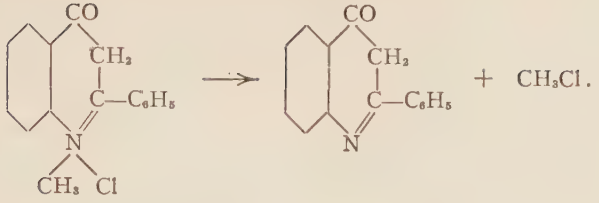
An interesting preparation [83] of dimethylvinyl-amine (boiling point 37°), in spite of small yields (0.3 gram from 10 grams), is its synthesis from neurine chloride, by distilling until the temperature of the vapor is 80°. Most of the salt chars in the process.

$$(CH_3)_3NCl{-}CH{=}CH_2 \longrightarrow CH_3Cl + (CH_3)_2N{-}CH{=}CH_2.$$

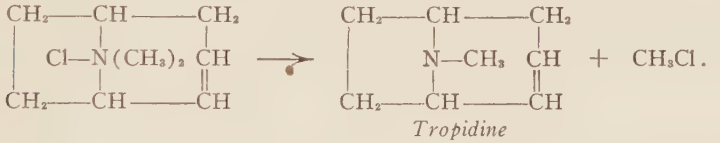
Two salts result [84] from the interaction of 1,2,3-tribromo-propene and trimethylamine; if either one is heated *in vacuo,* tribromopropene and trimethylamine may be recovered. Since methyl bromide is not lost, this is evidence that the dibromopropenyl group is less firmly attached to the nitrogen than the methyl. In this reaction, pyridine may be used interchangeably with trimethylamine.

With cyclic quaternary ammonium chlorides, the decomposition follows a similar course. Wherever possible, methyl chloride is quite generally eliminated. In the following pyrolysis,[85] the temperature is 250°:

[82] Reboul, *Compt. rend.* **93**, 69 (1881); **92**, 1422 (1881).
[83] Meyer and Hopff, *Ber.* **54**, 2274 (1921).
[84] von Braun and Kühn, *Ber.* **58**, 2168 (1925).
[85] Kaufmann and Plá y Janini, *Ber.* **44**, 2677 (1911).

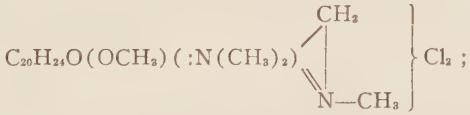


By heating[86] diquinoyl diethochloride in a vacuum, the two molecules of ethyl chloride are detached, and diquinoyl results. One of the steps in Willstätter's synthesis of tropine[87] from suberone involves the pyrolysis of a bicyclic quaternary ammonium chloride:

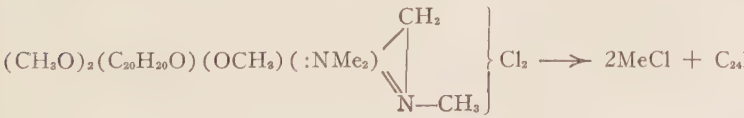


Tropidine

Such a process has recently been employed also in the strychnidine and brucidine series. Two apparently stereoisomeric[88] dimethochlorides of methoxymethyltetrahydrostrychnidine are assigned the formula:

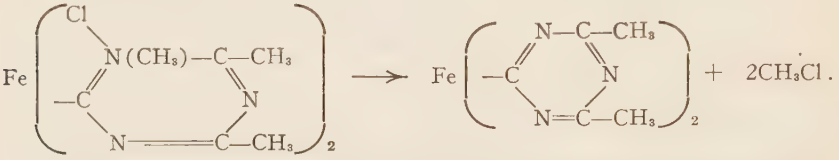


both evolve $2CH_3Cl$ on heating, but one gives methoxymethyltetrahydrostrychnidine, $C_{23}H_{32}O_2N_2$, whereas the other yields methyl-ψ-dihydrostrychnidine, $C_{22}H_{28}ON_2$. The latter compound may also be prepared by heating methyl-*neo*dihydrostrychnidinium chloride, $C_{22}H_{29}ON_2Cl$, and by a similar process with loss only of HCl, methyl*neo*strychnidinium chloride, $C_{22}H_{27}ON_2Cl$, may be converted into methyl-ψ-strychnidine. This is probably the best method of preparation of this substance. If methoxymethyl-dihydrobrucidine-methochloride is heated in 3-gram lots until the evolution of methyl chloride ceases, methyl-ψ-brucidine is formed in good yields; nine such runs give a yield of 16.5 grams:

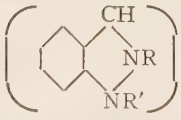


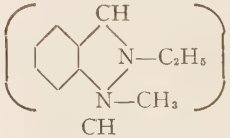
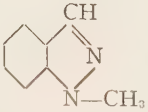
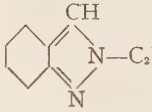
[86] Mills and Ordish, *J. Chem. Soc.* **1928**, 81.
[87] Willstatter, *Ber.* **34**, 129, 3164 (1901); *Ann.* **317**, 307 (1901); **326**, 1 (1903).
[88] Clemo, Perkin, Jr., and Robinson, *J. Chem. Soc.* **1927**, 1589; Gull, Perkin, Jr., and Robinson, *ibid.* p. 1627.

Methyl chloride [89] is also evolved in the following case at 140° in a vacuum, and after 2-3 hours, fairly pure tetramethyl-ferrocyanide constitutes the residue:



2,4,6-Triphenyl-pyridine interacts [90] with dimethyl sulfate at 100° to produce *N*-methyl-2,4,6-triphenyl-pyridinium-methyl-sulfate. At 174°, this quaternary salt reverts into dimethyl sulfate and triphenyl-pyridine. The corresponding quaternary chloride liberates methyl chloride and triphenyl-pyridine if it is slowly heated at 100°, but in a vacuum this transformation may be made to occur at a considerable lower temperature.

von Auwers has accumulated some interesting evidence relative to the firmness of attachment of the R—N bond in quaternary indazolium salts [91] of the type  , and of similar pyrazole derivatives. Salts of the first type undergo pyrolysis at 150-220° and 12 mm. into either RX or R′X. Admittedly, both nitrogen atoms are not of equal value with regard to the firmness of attachment, but since R and R′ may be interchanged the method is useful. In a general way, the firmness of the R—N bond was found to increase in the order of methyl, ethyl and propyl and, as before, allyl and benzyl were found easiest to be eliminated.

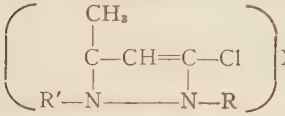
The following table gives in turn R, R′, X, and the percentage of 1-alkyl-indazole (R′-indazole) formed. The yield of 2-alkyl-indazole may be obtained by the difference from 100 percent. To illustrate: "Et, Me, I, 64 percent" means that in the distillation of  I, 64 percent of  and 36 percent of  are formed. Usually, these were isolated through the picrates.

[89] Hartley, *J. Chem. Soc.* **97**, 1725 (1910).
[90] Ziegler and Fries, *Ber.* **59**, 242 (1926).
[91] von Auwers and Pfuhl, *Ber.* **58**, 1360 (1925); von Auwers and Niemeyer, *J. prakt. Chem.* **110**, 153 (1925); von Auwers, Düsterdiek and Kleiner, *Ber.* **61**, 100 (1928).

TABLE XXXV. *Firmness of Attachment of the R—N Bond in Quaternary Indazolium Salts.*

R	R′	X	1-Alkyl-indazole Percent	R	R′	X	1-Alkyl-indazole Percent
Me	Me	I	92	Bu	Me	I	55
Me	Me	Br	95	{Me	Allyl	I	85
Me	Me	Cl	94	{Allyl	Me	I	100
{Me	Et	I	100	{Et	Allyl	I	43
{Et	Me	I	64	{Allyl	Et	I	100
Et	Me	Br	70	Pr	Allyl	I	26
{Me	Pr	I	100	{Me	Benzyl	I	84
{Pr	Me	I	40	{Benzyl	Me	I	100
Pr	Me	Br	52	Benzyl	Benzyl	I	100
Pr	Me	Cl	50	{Me	*o*-Chlorobenzyl	I	82
Et	Et	Br	Much	{*o*-Chlorobenzyl	Me	I	100
{Me	*iso*-Pr	I	100	{Me	*p*-Chlorobenzyl	I	96
{*iso*-Pr	Me	I	39	{*p*-Chlorobenzyl	Me	I	100
{Et	Pr	I	100	Pr	Pr	I	Much
{Pr	Et	I	100				

These data show definitely that a group in the 1-position is favored to stay, but that the nature of the group is also important. With the quaternary pyrazolium salts from 3-methyl-5-chloropyrazole,



X, the group R is usually eliminated as RX by distillation or vacuum distillation (in preference to R′X). This is always true with:

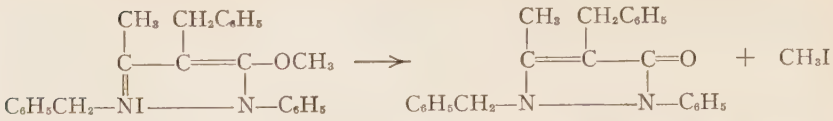
R′	R	X
CH_3	CH_3	I
CH_3	CH_3	Br
CH_3	C_2H_5	I
C_2H_5	CH_3	I
CH_3	$C_6H_5CH_2$	I

but with $C_6H_5CH_2$ CH_3 I, benzyl iodide is also eliminated. The pyrazole derivative which was isolated in the last case was

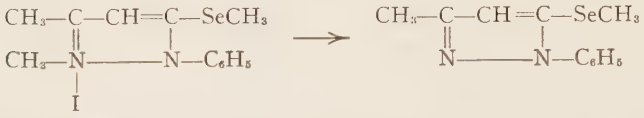
There are no data as yet for the allyl group.

von Auwers and Daniel [92] distilled 1-ethyl-2-propyl- and 1-propyl-2-ethyl- 3,5-dimethyl-pyrazolium iodide, and obtained a mixture of the two bases. When 1-benzyl-2-allyl-3-methyl-pyrazolium iodide is heated under atmospheric pressure, it pyrolyzes chiefly into 3-methylpyrazole but there is also some 1-allyl-3-methylpyrazole. Jacobson and Jost [93] reported the following reaction to occur at 234°:

[92] von Auwers and Daniel, *J. prakt. Chem.* **110**, 235 (1925).
[93] Jacobson and Jost, *Ann.* **400**, 213 (1913).



Similarly, selenopyrine-methiodide [94] becomes transformed into pseudo-selenopyrine (1-phenyl-3-methyl-5-selenomethyl-pyrazole) and methyl iodide, by heating at 180-200° at 11 mm. pressure.



Michaelis [95] has also performed similar experiments with the methiodide and the hydriodide of methyl-3-thiopyrene and of antithiopyrene.

A 67 percent yield of 4-nitro-1,2-dimethyl-glyoxaline [96] results from the distillation (at 33 mm.) of the following quaternary salt:

This is a reversal of the method of preparation of the salt. 4-Nitro-1,5-dimethyl-glyoxaline may be similarly prepared in 83 percent yields.

Arylammonium Halides.

Hofmann's position in organic chemistry is unusual since three different type reactions bear his name. In one of these, the essential feature is the wandering of the alkyl of an alkylated aniline hydrochloride from the nitrogen to a carbon of the nucleus under the influence of heat. Such, for example, is the conversion of methylaniline hydrochloride [97] into *p*-toluidine hydrochloride. Hofmann [98] suggested that methyl chloride was the active agent in the process, since his early experiments were performed by heating aniline-hydrochloride and methanol under pressure. Methylaniline hydrochloride was thereby formed at 230-250°, but after a day's heating at 350° there deposited, on cooling, a beautiful crystalline mass of toluidine hydrochloride.

Hofmann sensed the fact that his proposed mechanism of dissociation of methylaniline-hydrochloride into methyl chloride and aniline should lead to tertiary amines and eventually to quaternary salts. Tertiary amines were actually formed, but he found no evidence for the

[94] Michaelis and Duntze, *Ann.* **404**, 36 (1914).
[95] Michaelis and Drews, *Ann.* **350**, 326 (1906); Michaelis, Rademacher and Schmiedekampf, *Ann.* **354**, 55 (1907).
[96] Bhagwat and Pyman, *J. Chem. Soc.* **127**, 1832 (1925).
[97] Hofmann and Martius. *Ber.* **4**, 742 (1871).
[98] Hofmann, *Ber.* **5**, 720 (1872). *See also* Michaelis, *Ber.* **14**, 2107 (1881).

production of quaternary salts. However, he did find that phenyl-trimethyl-ammonium iodide undergoes pyrolysis from the quaternary salt into a mixture of the tertiary, secondary and primary salts. Fairly recent work by Howard and Derick [99] has established the essential accuracy of Hofmann's suggestion. In light of their work, it seems established that the mechanism of the Hofmann rearrangement requires a preliminary dissociation of methyl (or alkyl) chloride from methyl-aniline hydrochloride and subsequent addition to a second molecule until trimethylphenylammonium chloride is formed, and that this is the compound which rearranges.

Time is a factor in the rearrangement, but temperature is much more important. Recent work by Beckmann and Correns [100] shows that at 235°, distillation of methylaniline-hydrochloride gives no rearrangement. Similarly, after heating for 3 hours at 260° in a sealed tube, there is no evidence of toluidine, but Beckmann and Correns were able to demonstrate the presence of a mixture of equal parts of primary and secondary amines. Rearrangement into toluidine-hydrochloride occurs at 310° (4 hours in the tube), and tertiary amines are produced as well. Hofmann and Martius employed temperatures of 320-350°. According to Howard and Derick (*loc. cit.*), methylaniline-hydrochloride is partly changed into the hydrochlorides of primary and tertiary amines at temperatures below 250° in a sealed tube. Apparently, there is no formation of a quaternary salt, nor any rearrangement into a toluidine derivative unless the heating continues for 96 hours. At 300°, however, the quaternary compound, $C_6H_5N(CH_3)_3Cl$, may be isolated, and rearrangement begins.

Trimethylphenylammonium chloride [99] undergoes no rearrangement in 12 hours at 220-230°. Trimethylphenylammonium iodide appears to behave similarly, but rearranges [101] at somewhat lower temperatures. At 200°, it is unchanged, but at 220-230° rearrangement is apparent after a day's heating. Products such as $CH_3—C_6H_4N(CH_3)_2$, $(CH_3)_2C_6H_3NHCH_3$ and mesidine hydriodide, $2,4,6\text{-}(CH_3)_3C_6H_2NH_3I$ may be isolated if higher temperatures (335°, the melting point of lead) are used. In contrast, Winmill [102] points out the stability of the corresponding arsonium iodide, $C_6H_5As(CH_3)_3I$, even at 400°.

The best temperature [103] for the rearrangement of the salt from 1,2,4-xylidene and methyl iodide into mesidine hydriodide is 260°.

[99] Howard with Derick, *J. Am. Chem. Soc.* **46**, 166 (1924).
[100] Beckmann and Correns, *Ber.* **55**, 852 (1922).
[101] Hofmann, *Ber.* **5**, 706 (1872).
[102] Winmill, *J. Chem. Soc.* **101**, 718 (1912).
[103] Porter and Thurber, *J. Am. Chem. Soc.* **43**, 1197 (1921).

$$(CH_3)_2C_6H_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{NH_2I}} \longrightarrow (CH_3)_3C_6H_2—NH_3I.$$

No doubt the reaction in this case also proceeds through the quaternary salt. Above 260°, there is charring and below it, there is little change.

Ethyl-phenyl-ammonium chloride behaves [104] like the methyl compound. In a sealed tube (250-350°) there is rearrangement into $C_2H_5—C_6H_4—NH_3Cl$, preceded, however, by dissociation into aniline and ethyl chloride. From the work of Howard and Derick, it may be assumed that the intermediate formation of triethylphenylammonium chloride is a necessary prerequisite for the rearrangement. Between 220° and 290°, ethyl-phenyl-ammonium chloride [105] pyrolyzes chiefly into aniline, but there seems to be a small amount of another primary amine.

Experiments with butylaniline-hydrochloride [106] show that here again, there is a marked dissociation into *n*-butyl chloride and aniline. When heated in a retort for 100 hours at 280-300°, gases, condensed liquid and a tarry residue are obtained. The gas may have contained butylene, since small quantities of a dibromide were formed with bromine. From the condensed liquid, a small quantity of aniline-hydrochloride precipitated which was filtered off. After making the filtrate alkaline and redistilling, there was obtained *n*-butyl chloride (boiling point 77-80°), and a mixture of aniline and a secondary amine (boiling point 200-250°). The residue (in the retort) contained salts of primary and secondary amines, and diphenylamine derivatives were also considered to be present. Hickinbottom found that cobalt chloride, cadmium chloride and manganous chloride all catalyze the rearrangement of C_6H_5NHR into $R—C_6H_4—NH_2$.

When methyl-*n*-butyl-phenyl-ammonium chloride, $\underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{C_4H_9—NHCl—CH_3}}$ is heated in a stream of hydrogen chloride at 150-200°, it gives a residue which appears to contain the hydrochlorides of methyl aniline and of butyl aniline.

Ammonia is a dehalogenating agent [107] for organic chlorides at high temperatures (700-800°). In many cases, the halogen is eliminated quantitatively as ammonium chloride, but with some aromatic halides, there results only 70 percent of the theoretical amount.

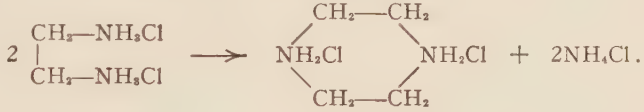
[104] Hofmann, *Ber.* **7**, 526 (1874); Lauth, *Ber.* **6**, 677 (1873).
[105] Hickinbottom, *J. Chem. Soc.* **1927**, 64.
[106] Reilly and Hickinbottom, *ibid.* **117**, 128 (1920).
[107] Heslinga, *Rec. trav. chim.* **43**, 178 (1924).

Halides of the Diamines.

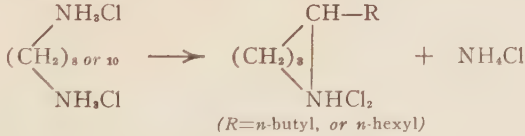
A very convenient way to prepare heterocyclic compounds containing nitrogen is to subject the hydrochlorides (mono or di) of diamines to dry distillation. Pyrrolidine [108] and piperidene may thus be readily obtained:

$$ClNH_3—(CH_2)_4—NH_3Cl \longrightarrow NH_4Cl + (CH_2)_4{=}NH_2Cl$$
$$ClNH_3—(CH_2)_5—NH_3Cl \longrightarrow NH_4Cl + (CH_2)_5{=}NH_2Cl$$
(18 grams) *(8 grams)*

It is impossible by this method to obtain the three-membered ring compound, ethylene imine, by distilling [109] the hydrochloride of ethylene diamine; instead, piperazine hydrochloride is produced:



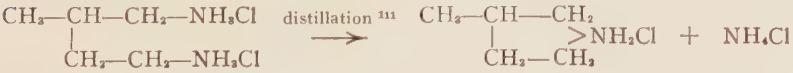
The formation of the 5- or the 6-membered ring is always favored. To illustrate this point, it may be noted that substituted pyrrolidines (5-membered ring) are formed [110] from octylene- and decylene-diamine hydrochlorides, instead of the compounds which might be anticipated with 9 or 11 members in the ring:



(R=n-butyl, or n-hexyl)

Seven-membered rings may be formed, however.

Other illustrations which undergo the usual type reaction are:

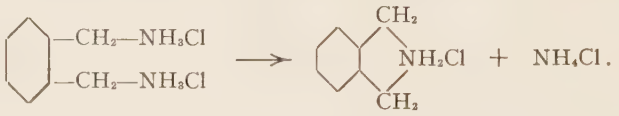


and [112]

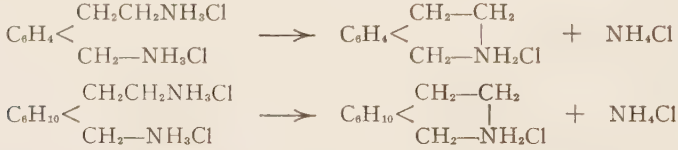
Urazole

[108] Ladenburg, *Ber.* **18**, 3100 (1885); **20**, 442 (1887); Ladenburg and Sieber, *Ber.* **23**, 2727 (1890).
[109] Ladenburg and Abel, *Ber.* **21**, 758 (1888); **23**, 3740 (1890); Majert and Schmidt, *Ber.* **23**, 2721 (1890).
[110] Blaise and Houillon, *Compt. rend.* **142**, 1541 (1906); **143**, 361 (1906).
[111] Oldach, *Ber.* **20**, 1657 (1887).
[112] Pellizari and Cuneo, *Gazz. chim. ital.* **24**, I, 499 (1894); Thiele and Uhlfelder, *Ann.* **303**, 94 (1898).

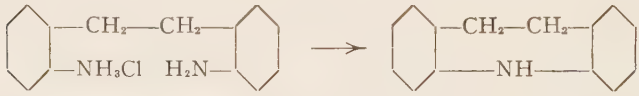
Five, six, and sometimes seven-membered rings are easily formed in entirely analogous reactions from aromatic diamines. For example, the preparation [113] of dihydro*iso*indole from the hydrochloride of *o*-xylylene-diamine by thermal means was employed to prove the constitution of the former compound:



A 58 percent yield of tetrahydro*iso*quinoline, and a 50 percent yield of decahydro*iso*quinoline, by pyrolysis [114] of the salts of homo-*o*-xylylene-diamine and homo-*o*-hexahydro-xylenediamine respectively have been recently reported.



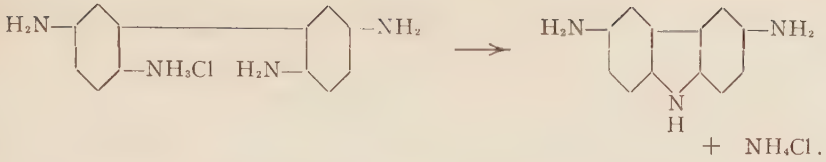
o-Imino-dibenzyl [115] is formed in good yields (60 percent, after purification) when 2,2′-diamino-dibenzyl is heated for 26-30 hours at 265-275° with its hydrochloride:



Carbazole [116] is formed quantitatively at 200° in a reaction of this type:

It is well to point out that when the ring closure is effected by this means between two aromatic nuclei, the amino groups are always situated on *ortho* carbon atoms, or they are attached to an *ortho* side chain. Thus, when 2,2′,5,5′-tetraaminodiphenyl [117] is heated (10 hours at 180°) with hydrochloric acid, only the 2,2′-amino groups enter the reaction:

[113] Gabriel and Pinkus, *Ber.* **26**, 2213 (1893).
[114] Helfer, *Helv. Chim. Acta* **6**, 785 (1923).
[115] Thiele and Holzinger, *Ann.* **305**, 100 (1899).
[116] Täuber, *Ber.* **24**, 200 (1891).
[117] Täuber, *Ber.* **25**, 131 (1892).

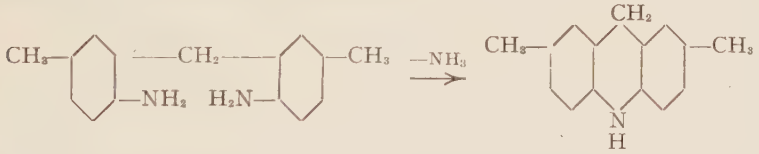


The preparation of diphenylamine by heating a mixture of aniline and aniline hydrochloride is a reaction [118] which is entirely parallel to the ones which have been mentioned, save that the two amino groups are not in the same molecule:

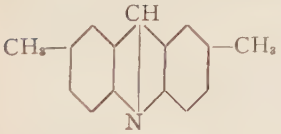
$$C_6H_5NH_2 + C_6H_5NH_3Cl \longrightarrow NH_4Cl + (C_6H_5)_2NH.$$

Diphenylamine hydrochloride sublimes [119] without decomposition at 250°.

Ullmann [120] has furnished an interesting means of deammonation for diamino-ditolylmethane and similar compounds. The base (20 grams) is fused in a mixture of *p*-toluidine (20 grams) and *p*-toluidine-hydrochloride (40-50 grams) at 200-220° for 1 hour. Ammonium chloride precipitates from the melt, and a yield of 5.5 grams of 2,7-dimethyldihydroacridine is obtainable.



There is also formed an equal weight of 2,7-dimethylacridine,

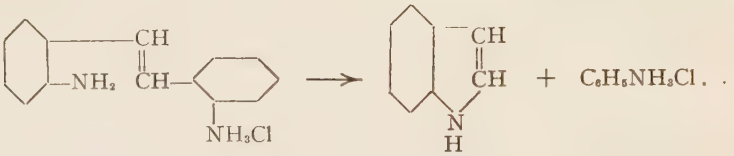


.

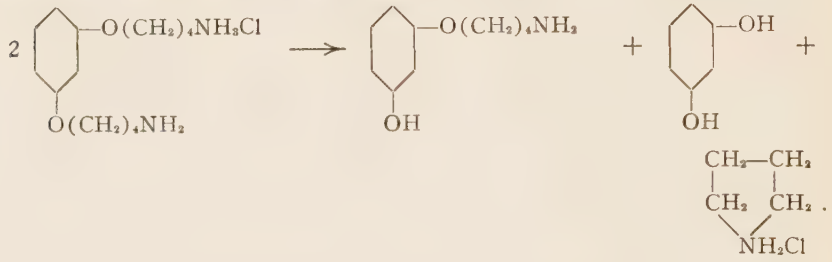
In some cases, ammonium chloride is not the product of the reaction in the pyrolysis of a diamino-hydrochloride. However, in such cases, the molecule is more profoundly altered and instead of a large heterocyclic ring, a ring of five atoms usually results. A case to illustrate this point [121] is 2,2′-diamino-stilbene. This is very closely related in structure to 2,2′-diamino-dibenzyl (p. 326), yet the two substances behave quite differently when heated. When a mixture of 2,2′-diamino-stilbene and its hydrochloride is heated at 170-180°, aniline-hydro-

[118] de Laire, Girard and Chapoteaut, *Z. Chemie* **1866**, 438.
[119] Lachman, *J. Am. Chem. Soc.* **46**, 1482 (1924).
[120] Ullmann, *Ber.* **36**, 1017 (1903).
[121] Thiele and Dimroth, *Ber.* **28**, 1411 (1895).

chloride and indole are formed quantitatively. This may be represented as follows:

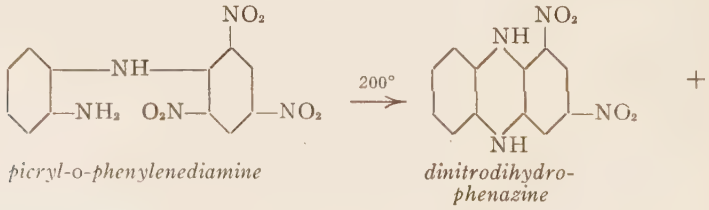


The pyrolysis of resorcinol-bis-(δ-aminobutyl) ether hydrochloride [122] at 7-15 mm. and 160-265° gives rise to resorcinol, pyrrolidine-hydrochloride and resorcinol-mono-δ-aminobutyl ether; there is absolutely no indication of any *meta* ring closure in this reaction.



Miscellaneous Derivatives of Amines.

The following interesting decomposition [123] occurs in molten naphthalene:

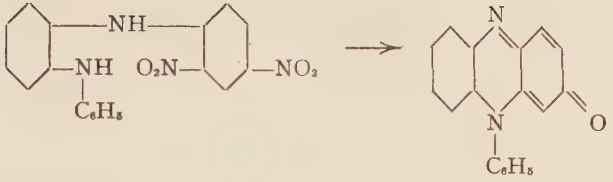


picryl-o-phenylenediamine — *dinitrodihydrophenazine*

HNO_2 (or decomposition products)

In this reaction, nitrous fumes are evolved copiously, and there may be isolated a yield of 0.4 gram of the phenazine from 2 grams of the original substance. Somewhat similar is the following conversion,[124] which is also accompanied by nitrous fumes (apparently HNO_2 and HNO are eliminated), when the nitro compound (1 gram) is heated in benzoic acid (20 grams), or when it is heated in benzil.[125] Kehrmann believed that the benzil and the benzoic acid served only as solvents.

[122] Wilson with Adams, *J. Am. Chem. Soc.* **45**, 529, 535 (1923).
[123] Leeman and Grandmougen, *Ber.* **41**, 1309 (1908).
[124] Kehrmann and Bürgin, *Ber.* **29**, 1819 (1896).
[125] Kehrmann and Messinger, *J. prakt. Chem.* [2] **46**, 572 (1892).



The benzal amines have already been mentioned (p. 102); they are pyrogenically decomposed at red heat. Reference may also be made to the production of flavanthrene at 250° from 2,2′-diamino-1,1′-dianthraquinonyl (p. 41). Flavanthrene is a compound that bears somewhat of a structural similarity to the benzal amines, and is undoubtedly quite resistant to pyrolytic changes.

Trimethyl azonium hydroxide, $(CH_3)_3N<^{NH_2}_{OH}$, undergoes pyrolysis [126] by distillation at 150 mm., and yields *unsymmetrical* dimethyl hydrazine (20 percent), dimethyl-amine, ammonia, and a lachrymatory compound.

In the reaction [127] of $R_2C{=}N{-}C_6H_5 + H_2N{-}Ar$, giving $R_2C{=}NAr + C_6H_5NH_2$, the intermediate compound of the type: $R_2C<^{NH{-}C_6H_5}_{NH{-}Ar}$, may be formed. As indicated, it decomposes by vacuum distillation. The course of the decomposition may be influenced by the greater volatility of aniline, or by the greater concentration of $ArNH_2$. The intermediate compound possesses an unstable grouping (see p. 21).

[126] Harries and Haga, *Ber.* **31**, 58 (1898).
[127] Reddelien, *Ber.* **54**, 3121 (1921).

CHAPTER 13.

MONOBASIC ACIDS.

The decarboxylation reaction of monobasic acids:

$$R—CO_2H \longrightarrow R—H + CO_2,$$

is undoubtedly a most general reaction insofar as pyrolysis is concerned. In cases where the reaction proceeds with difficulty by heat alone, it may be assisted by heating in the presence of soda-lime or of sodium hydroxide. Possibly the best known case of this type is the dry distillation of a mixture of sodium acetate and sodium hydroxide, as a laboratory method for the preparation of methane:

$$CH_3—CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4.$$

The methane formed in such a reaction is far from pure, but is contaminated with hydrogen and other hydrocarbons.

Except in the presence of catalysts (metallic oxides or carbonates), acids do not eliminate carbonic acid to produce ketones:

$$2R—CO_2H \longrightarrow CO_2 + H_2O + R_2CO.$$

Since ketones may be formed by heating certain salts of these acids, it may be that the function of the catalyst is to convert the acid temporarily into the salt which, however, is unstable at the temperature of the reaction (see p. 193). Ketones are formed, many times in excellent yields. Other possible modes of pyrolysis of acids will be taken up in their proper place with the acids concerned.

The monobasic acids will be discussed in the following order: aliphatic, substituted-acetic acids, aromatic acids, unsaturated acids, ketonic acids, *O*-heterocyclic acids, lactonic acids, *N*-heterocyclic acids.

Aliphatic Acids.

Formic Acid.

Berthelot [1] reported that during the first half of its thermal decomposition, formic acid gives off carbon monoxide and water, whereas at the completion there is also formed some carbon dioxide and hydrogen. Engler stated that at 169°, formic acid [2] is completely transformed into

[1] Berthelot, *Ann. chim. phys.* [4] **18**, 42 (1869).
[2] Engler and Grimm, *Ber.* **30**, 2922 (1897).

water and carbon monoxide. Ten cc. of the acid, in 8 hours at 150-160°, gives 300 cc. of gas which is 98.8 percent carbon monoxide and 1.2 percent carbon dioxide. Somewhat later, Nef reported [3] that the gaseous products from the pyrolysis of formic acid over pumice at 570° contain only 6.4 percent carbon monoxide, but 46.4 percent carbon dioxide and 47.2 percent hydrogen.

It is readily seen that formic acid can decompose like an acid into carbon dioxide, or like an aldehyde into carbon monoxide.

As an acid:

$$H{-}CO_2H \longrightarrow H_2 + CO_2$$

As an aldehyde:

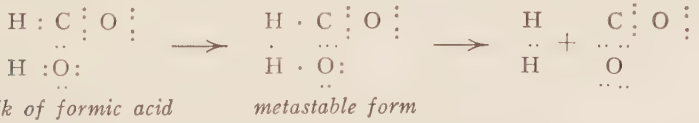
$$H{-}O{-}CHO \longrightarrow H_2O + CO$$

Which of these two reactions predominates, therefore, depends upon conditions.

Muller and Peytral passed formic acid [4] through a short platinum tube at 1150°, and considered the primary reaction to be to hydrogen and carbon dioxide. Inasmuch as the ratio of $CO_2 : CO$ varied with varying factors it was concluded that the CO was formed as a result of the secondary reaction:

$$H_2 + CO_2 \longrightarrow H_2O + CO.$$

Small amounts of methane, ethylene and acetylene were also formed. Still more recently,[5] these investigators have defended this interpretation by a mathematical treatment of the data. They find that the first reaction, the one into $H_2 + CO_2$, is complete in 0.01 second, and that the mol fraction of CO_2 formed in a given time interval minus the mol fraction decomposed equals 0.49 ± 0.01, after an initial time interval of 0.002 sec. All calculations are based on a time interval of 0.01 sec. Müller assumes that the decomposition of formic acid [6] into hydrogen and carbon dioxide proceeds through a metastable form. This is represented as follows:



bulk of formic acid *metastable form*

A study [7] of the pyrolysis of formic acid in pyrex, porcelain, silica and copper tubes between 350 and 600° shows the principal reaction to

[3] Nef, *Ann.* **318**, 221 (1901).
[4] Muller and Peytral, *Bull. soc. chim.* **29**, 34 (1921).
[5] *Ibid.*, **39**, 995 (1926).
[6] E. Müller, *Z. Elektrochem.* **31**, 46 (1925).
[7] Nelson and Engelder, *J. Phys. Chem.* **30**, 470 (1926).

be into hydrogen and carbon dioxide, with a minor reaction into formaldehyde:

$$2HCO_2H \longrightarrow CO_2 + H_2O + HCHO.$$

Nelson and Engelder believe that the carbon monoxide which is formed comes both from the formic acid and from the formaldehyde. At 450°, the transformations are over 90 percent complete. Pyrex tubes show the least catalytic activity and copper the most; silica tubes become more active by etching. At 170° the formic acid is found [8] to decompose exceedingly slowly. This does not agree with the earlier statement of Engler and Grimm, but it does agree with the fact that large amounts of formic acid may be isolated from the pyrolysis of oxalic acid at 120-170° (see p. 392).

Hinshelwood [9] has given the subject of formic acid pyrolysis a fairly satisfactory treatment. He considers the two reactions of formic acid (into $CO_2 + H_2$, and into $CO + H_2O$) to be quite independent reactions. Between temperatures of 138-350°, the relative velocities of the two reactions vary considerably with the nature of the glass surface, and they differ even in two quite similar bulbs. In Jena glass apparatus, there is always less hydrogen than carbon dioxide, indicating that the reaction:

$$2HCO_2H \longrightarrow HCHO + CO_2 + H_2O$$

proceeds to a slight extent. It was shown that even at 350°, carbon monoxide and water do not interact.

Acetic Acid.

The thermostability of acetic acid was noticed by Cahours [10] and by Berthelot,[11] who showed that it did not decompose below a dull red heat. *Propionic, n-* and *isobutyric,* and *isovaleric* acids are also stable [12] to a temperature of 460°. Engler and Löw [13] found that both acetic and benzoic acids are stable in a sealed tube at 390°, whereas under similar conditions butyric and caproic acids suffer no more than a slight pyrolysis at 370°. At a dark red glow, other investigators [14] found acetic acid to pyrolyze into carbon dioxide and methane, as well as to acetone, carbon dioxide and water. Oppenheim and Precht actually studied ethyl acetate and not acetic acid. At a "somewhat lower temperature than

[8] Noyes, Jr., and Wobbe, *J. Am. Chem. Soc.* **48**, 1882 (1926).
[9] Hinshelwood, Hartley and Topley, *Proc. Roy. Soc.* (London) **100A**, 575 (1922); Hinshelwood and Hartley, *J. Chem. Soc.* **123**, 1333 (1923).
[10] Cahours, *Compt. rend.* **19**, 771 (1844); **20**, 51 (1845).
[11] Berthelot, *Ann. chim. phys.* [3] **33**, 295 (1851); **53**, 187 (1858).
[12] Senderens and Aboulenc, *Compt. rend.* **170**, 1064 (1920).
[13] Engler and Löw, *Ber.* **26**, 1439 (1893).
[14] Oppenheim and Precht, *Ber.* **9**, 325 (1876).

dull red glow", ethylene and acetic acid were the isolated products. Thus, they reasoned that at "dull red glow", the acetic acid was actually decomposing into the products mentioned.

Nef [3] observed much carbonization when acetic acid vapors were passed over pumice at 500°, and he also reported a high concentration of carbon monoxide in the gas. In part, the latter may have been formed by the interaction of carbon and carbon dioxide. However, charcoal has been found [12] to catalyze the decomposition of aliphatic acids at 360-380° and carbon monoxide is an important product of the decomposition. Nef's data follow: acetic acid used, 30 grams; duration of experiment, 45 min.; gaseous products, other than carbon dioxide and ethylene, 5 liters, of which 58.6 percent is methane, 34 percent carbon monoxide, and 7.4 percent hydrogen; the weight of ethylene bromide, which is indicative of the ethylene formed, is 2.5 grams; acetone, identified as 0.6 gram of acetone oxime, concludes the list.

Recently,[15] it has been found that the anhydrides of acetic, propionic or butyric acids may be formed by passing the vapors of the respective acids over fireclay at 650°, and chilling the vapors quickly. It is stated to be beneficial to add indifferent hydrocarbon vapors as a diluent to precipitate the water which forms. In another recent patent, dealing with the formation of acetic anhydride and water from acetic acid,[16] the acid is heated to 400-800° in the absence of base metals and metal oxides.

Superficially, it may excite no wonder to learn that acetic anhydride may be prepared from acetic acid by heat alone. However, no other monobasic acid in organic chemistry behaves in this manner; therefore, some unusual feature must be present in this case more than is implied by the mere presence of the carboxyl group. Under the heading of the "methane system" (p. 25) there was developed an analogy between carbonic acid, acetic acid and acetone in their behavior towards heat. Thus, carbonic acid, with its two hydroxyls, eliminates water, whereas acetone, with its two methyls, eliminates methane:

$$HO—CO—OH \longrightarrow H_2O + O{=}C{=}O\,; \quad \text{and}$$
$$CH_3—CO—CH_3 \longrightarrow CH_4 + CH_2{=}C{=}O\,.$$

The other two products, respectively, are carbon dioxide and ketene. Both of these products might be anticipated from acetic acid, since it

[15] Consortium für Elektrochemische Industrie, Brit. Pat. 194,719, March 10, 1923; *Chem. Abstracts* **17**, 3509 (1923).
[16] Meingast and Mugdam, U. S. Pat. 1,570,514, Jan. 19, 1926; *Chem. Abstracts* **20**, 768 (1926).

contains one methyl and one hydroxyl, instead of two methyls or two hydroxyls.

$$CH_3—CO—OH \rightleftharpoons \begin{matrix} CH_4 + O{=}C{=}O \\ H_2O + CH_2{=}C{=}O \end{matrix}$$

Recent experiments [17] in the author's laboratory have demonstrated the correctness of this method of reasoning. By passing acetic acid vapors through a silica tube, packed with broken porcelain, at 800° C., appreciable amounts of ketene may be identified in the outgoing vapors, providing the latter are rapidly cooled in such a manner that the high-boiling materials (acetic acid, acetic anhydride, water) are constantly condensed and withdrawn to prevent unnecessary contact with the ketene. This, therefore, furnishes the clue to explain the formation of acetic anhydride during the pyrolysis of acetic acid. It comes merely by interaction of ketene and acetic acid:

$$CH_3CO—OH \longrightarrow CH_2{=}C{=}O \xrightarrow{CH_3CO_2H} CH_3CO—O—COCH_3.$$

Furthermore, this reaction mechanism provides a convenient explanation to account for a part of the carbon monoxide which is produced, since ketene undergoes scission into ethylene and carbon monoxide.

Mlle. Peytral's evidence, obtained [18] by passing acetic acid through a platinum tube 11 cm. long at 1150°, is well explained by the above mechanism. Instead, she postulated three first-order reactions to explain the results:

$$2CH_3CO_2H \longrightarrow H_2O + (CH_3CO)_2O$$
$$CH_3CO_2H \longrightarrow CO_2 + CH_4$$
$$2CH_3CO_2H \longrightarrow 2H_2O + 2CO + C_2H_4$$

With a rate of flow of 0.088 gram per sec., 18.1 grams of acetic acid gives 17.9 grams of condensed liquids, only 3.17 grams of which boils above 118.6. This contains 0.31 gram of anhydride. It was thought that part of the anhydride underwent pyrolysis into water, carbon monoxide and ethylene. Analysis of the gases gives figures resembling Nef's: methane, 38.7 percent; carbon dioxide, 34.8 percent; carbon monoxide, 16 percent; ethylene, 5.6 percent; and hydrogen, 4.9 percent. Data were also presented for rates of flow of 0.044, 0.035 and 0.02 gram per second. At these slower rates, some acetylene appears; also there is a greater quantity of carbon monoxide and of hydrogen, which increment was thought by Mlle. Peytral to be caused by an interaction of carbon dioxide and methane. Presumably, the acetylene comes from the ethylene. It was calculated that 6.1 mols of acetic acid pyrolyzed in

[17] Hurd and Martin, unpublished results.
[18] Peytral, *Bull. soc. chim.* [4] **31**, 113 (1922).

accordance with the first reaction; 2.96 with the second reaction; and 0.79 with the third reaction.

The pyrolytic behavior of *homologs of acetic acid* was investigated by Nef (Reference 3). Except for a temperature of 600°, the method was comparable to his method with acetic acid. With propionic acid, and presumably with the others, there was carbonization. The data are given in Table XXXVI, and for convenience, acetic acid is also listed. The condensate in each case was chiefly recovered acid and water. A croton-aldehyde odor was reported with propionic acid and *n*-butyric acid; a small quantity of *iso*butyraldehyde (0.6 gram) was thought to be present in the *iso*valeric acid condensate, and from *iso*butyric as well as acetic acid, a little acetone was found.

TABLE XXXVI. *Pyrolysis of Acetic Acid and Its Homologs.*

Acid, and Quantity Grams	Time Minutes	Rate, Grams per Minute	Condensate	Unrecovered Acid	Olefine Bromides	CO_2 in Total Gas Percent	Volume CO, H_2, C_nH_{2n+2} Liters	CH_4	CO	H_2	C_2H_6
			Grams					Percent			
acetic 30	45	0.66	?	?	2.5	?	5.0	58.6	34.0	7.4	...
propionic 30	40	0.75	14.8	20.0	12.5 calcd. as 2 liters C_2H_4	16.33	5.0	19.5	50.8	20.0	9.75
n-butyric 60.1	120	0.50	20.0	48.2	58.7	20.3	14.4	47.8	37.9	11.2	3.05
iso-butyric 70	90	0.77	42.3	35.8	43.6	16.0	11.5	29.6	46.3	22.2	1.9
iso-valeric 70	60	1.16	37.2	43.4	51.7	17.0	10.1	49.0	32.3	15.1	3.7

The olefine from acetic acid and propionic acid was exclusively ethylene. With the other three, distillation analysis showed a rather complex mixture up to, and in each case including, divinyl.

The normal fatty acids may be distilled at ordinary pressure up to about C_{12}, and the higher members may be distilled in a vacuum. If *stearic* acid[19] is heated alone in an iron vessel for 4 hours, there is formed a 91 percent yield of ketone, which may be made nearly quantitative by longer heating. In small quantities, the reaction completes itself in 3 hours. *Palmitic acid* undergoes a similar quantitative reaction in 3 hours at 295°; *myristic acid*, at 285°; and *lauric acid* at 270°. Of interest from a viewpoint regarding the genesis of petroleum, is Neuberg's

[19] Grün, Ulbrich and Krczil, *Z. angew. Chem.* **39**, 421 (1926).

experiment [20] in which he heated a mixture of valeric and oleic acids (1:8) for 16 hours at 350° in a sealed tube. At 4-hour intervals, the tubes were opened to release the pressure. After removal of acids, aldehydes and ketones from the light yellow fluid which was formed, there remained an optically active oil, with a naphtha odor, which gave the cholesterol test.

Substituted Acetic Acids.

There is a considerable mass of data dealing with the elimination of carbon dioxide from substituted acetic acids, $Y—CH_2—CO_2H$. What evidence there is seems to point to the fact that the electron attraction series (p. 26) may be highly useful in enabling one to catalog these data. In general, if Y is a positive radical such as benzyl, the acid is fairly stable towards heat, whereas if Y is a negative radical such as phenyl, or cyano, or carboxyl, there is a much greater tendency for the decarboxylation reaction. The details of a few cases will be presented, and the others will merely be tabulated.

Toluene is formed in 70 percent yields when phenylacetic acid [21] is heated in a sealed tube for 5 hours at 340-370°, and then, after releasing the pressure, for 10 hours more at 355-375°. At the conclusion of the experiment, the pressure in the tube was found to be 10 atmospheres. In addition to toluene, there is a 10 percent yield of dibenzyl ketone, and a little carbon monoxide. The chief reaction, therefore, is

$$C_6H_5—CH_2—CO_2H \longrightarrow C_6H_5CH_3 + CO_2,$$

and the other apparent reaction is:

$$2C_6H_5CH_2CO_2H \longrightarrow (C_6H_5CH_2)_2CO + CO_2 + H_2O.$$

Between 90 and 99.5 percent of the gas is carbon dioxide. Engler demonstrated that pressure was without material effect on the pyrolysis, when he obtained similar results at 375° in a very large tube which had been completely evacuated prior to the heating. Phenylacetic acid is unattacked at 320-330° if the acid is passed at that temperature through a porcelain-filled glass tube.

Hydrocinnamic acid, $C_6H_5CH_2—CH_2CO_2H$, is much more stable than phenylacetic acid. It suffers only slight decomposition in a sealed tube at 370°. Some gas is formed, but ethyl benzene is not isolable. The gas is 90-95 percent carbondioxide and the remainder carbon monoxide. In contrast, the isomeric hydratropic acid, $\begin{matrix} & C_6H_5 \\ & | \\ CH_3— & CH— \end{matrix}CO_2H$, undergoes

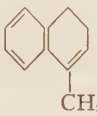
[20] Neuberg, *Biochem. Z.* 7, 199 (1908).
[21] Engler and Löw, *Ber.* 26, 1436 (1893).

pyrolysis very readily. It is over 90 percent decomposed after five repeated pressure distillations. The negative groups on the α-carbon atom would lead one to expect this behavior. Yet more striking is the fact that dinitrocinnamic acid breaks down into carbon dioxide and dinitrostyrene even at 0°.

It is apparent that the benzal group in cinnamic acid is more negative than the benzyl group in hydrocinnamic. Thus, cinnamic acid should be relatively unstable and this is found to be the case. The remarkable instability of dinitrocinnamic acid (with the very negative dinitrobenzyl group) is also in keeping with this line of reasoning. Furthermore, it would be anticipated that derivatives of propiolic acid, R—C≡C—CO_2H, should be rather easily decarboxylated into an acetylene. Actually, phenylpropiolic acid is changed into phenylacetylene at 120° (in water solution); and nitrophenylpropiolic acid [22] at 100°. *p*-Tolylpropiolic acid [23] readily undergoes pyrolysis into *p*-tolyl-acetylene.

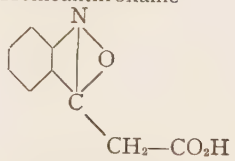
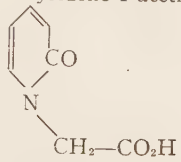
Malonic acid is an excellent illustration of the effect of an α-negative group. It, and its homologs, pyrolyze very smoothly into acetic acid or its derivatives. With succinic acid, this tendency becomes practically negligible. Another case, which is very well known is acetoacetic acid, $CH_3CO—CH_2CO_2H$. It need only be mentioned that the α-acetyl group is a negative group. These cases and others will be treated in more detail in later pages.

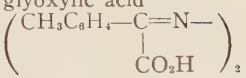
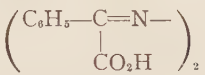
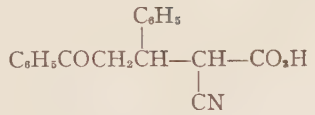
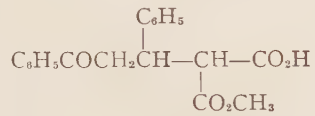
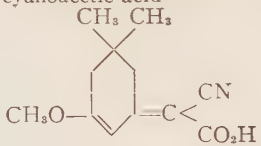
At 270°-300°, α,α-dinaphthylacetic acid undergoes pyrolysis [24] into α,α-dinaphthylmethane and carbon dioxide, and β,β-dinaphthylacetic acid begins [25] to lose carbon dioxide at 200°. A similar decomposition of diphenylene-alkyl-acetic acid, $(C_6H_4)_2CR—CO_2H$, occurs at 250°. In this case,[26] *R* represents methyl, ethyl, benzyl or allyl. Above its melting point,[27] 246°, diphenyl-*p*-carboxyphenyl-acetic acid evolves carbon dioxide.

Similarly,[28] with Δ^5-dihydronaphthyl-5-acetic acid,  , at

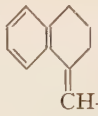
[22] Engler and Löw, *ibid*, p. 1441.
[23] Gattermann, *Ann.* **347**, 359 (1906).
[24] Schmidlin and Bergman, *Ber.* **43**, 2824 (1910).
[25] Schmidlin and Huber, *Ber.* **43**, 2835 (1910).
[26] Wislicenus and Mocker, *Ber.* **46**, 2772 (1913).
[27] Jones and Root, *J. Am. Chem. Soc.* **48**, 185 (1926).
[28] Schroeter, *Ber.* **58**, 713 (1925).

TABLE XXXVII. *Pyrolysis of Substituted Acetic Acids.*

Acid	Temperature for Carbondioxide Elimination °C.	Other Product	Yield	Reference
Homoanthroxanic 	120° (stormily)	Methyl-anthroxan	Good	Heller and Tischner, *Ber.* **42**, 4555 (1909).
2-Pyridone-1-acetic 	Above 200°	*N*-methyl-α-pyridone	....	Kirpal, *Ber.* **57**, 1954 (1924).
Oximino acids $CH_3CO—C(=NOH)—CH_2CO_2H$	119°	$CH_3CO—C(=NOH)—CH_3$	....	Thal, *Ber.* **25**, 1719 (1892).
α-$C_{10}H_7—C(=NOH)—CO_2H$	Vacuum distillation	α-$C_{10}H_7—CN + H_2O$	....	Rousset, *Compt. rend.* **123**, 60 (1896).

Azine of *p*-cresylglyoxylic acid 	200°	Azine of *p*-toluylaldehyde	....	Bouveault, *Compt. rend.* **122**, 1491 (1895).
	180-200° 1 hour	$(C_6H_5—CH=N—)_2$	....	Bouveault, *Bull. soc. chim.* **15**, 1019 (1896).
*Nitroacetic	87-89°	Nitromethane	....	Steinkopf, *Ber.* **42**, 3929 (1909).
Cyanoacetic acid	165°	Acetonitrile	....	van't Hoff, *Ber.* **7**, 1382 (1874).
	200°	γ-benzoyl-β-phenylbutyronitrile	High yield	Kohler, Graustein, Merrill, *J. Am. Chem. Soc.* **44**, 2543 (1922).
	180-200°	Methyl benzoylphenylbutyrate	High yield	*Ibid.*
3-Methoxy-1,1-dimethyl-Δ^3-cyclohexenylidene-5-cyanoacetic acid 	179°	Methoxy-dimethylcyclohexenylidene-acetonitrile	....	Crossley and Gilling, *J. Chem. Soc.* **97**, 530 (1910).

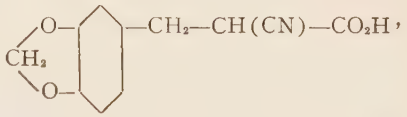
* For the kinetics of this decomposition, see Pedersen, *Trans. Faraday Soc.* **23**, 316 (1927); *Chem. Abstracts* **22**, 1068 (1928). Nitromethane is best prepared by heating the sodium salt of nitroacetic acid in water solution at 85-90°; yield, 35-38 percent. "Organic Syntheses," New York, John Wiley and Sons, Inc., **1923**, p. 83.

152-5° and 5-tetralylene-acetic acid,  , at 140°, there is

carbon dioxide elimination. Rather surprisingly, a quantitative elimination of this gas also occurred on short boiling with dilute sulfuric acid. The hydrocarbons, 5-methyl-7,8-dihydronaphthalene and 5-tetralylene-methane, are formed respectively.

Similar data for other substituted acetic acids are briefly presented in Table XXXVII.

In the last case in the table, there is a steady evolution of CO_2 at about 5° above the melting point, and the corresponding acetonitrile forms in excellent yields. The analogous ethoxy compound melts at 149°, and pyrolyzes steadily in a similar fashion at 153°. In some cases with α-cyano acids, it has been found that copper powder or copper bronze is an efficient catalyst, and this is especially helpful in cases where charring would otherwise occur in the thermal decomposition. Thus,

α-cyano-β-piperonyl-propionic acid,  ,

if mixed with one-fifth of its weight of copper bronze, is rapidly decomposed into the nitrile [29] by heating. Another such case, in which twice the weight of copper powder is used, is cyanocinnamenyl-acrylic acid,[30] $C_6H_5CH{=}CH{-}CH{=}C(CN){-}CO_2H$, at 210°.

α-Sulfone acids are easily decarboxylated, a fact which is in keeping with the influence exerted by an α-negative group. Illustrative [31] of this, α-ethylsulfone-propionic acid gives diethyl sulfone easily at 200°:

$$C_2H_5{-}SO_2{-}CH(CH_3){-}CO_2H \longrightarrow CO_2 + C_2H_5{-}SO_2{-}C_2H_5.$$

The isomeric β-ethylsulfone-propionic acid, $C_2H_5{-}SO_2{-}CH_2CH_2{-}CO_2H$, is much more stable. It should be noticed that the negative sulfone group is no longer attached to the α-carbon. Sulfoacetic acid, $HO_3S{-}CH_2{-}CO_2H$, evolves carbon dioxide [32] at 190°, but the decomposition is fairly complex, for acetic acid also distils in the process and at 210° sulfur dioxide is formed. Franchimont gives the following equations:

$$HO_2C{-}CH_2{-}SO_3H \longrightarrow SO_3 + CH_3{-}CO_2H,$$

[29] Baker and Robertson, *J. Chem. Soc.* **127**, 1424 (1925).
[30] Rinkes, *Rec. trav. chim.* **39**, 200 (1920).
[31] R. and W. Otto, *Ber.* **21**, 992 (1888).
[32] Melsens, *Ann.* **52**, 277 (1844); Franchimont, *Rec. trav. chim.* **7**, 25 (1888).

and then

$$SO_3 + HO_2C{-}CH_2{-}SO_3H \longrightarrow CO_2 + CH_2(SO_3H)_2.$$

Monochloro- and dichloro-acetic acids were investigated [33] by Engler and Steude who merely reported that the decomposition was not smooth. Presumably, the conditions of their work were a temperature of 300° in a sealed tube. Previously, it had been shown [34] that formaldehyde was one of the decomposition products when monochloroacetic acid is passed through a hot tube. In spite of the accumulation of negative chlorine groups, *trichloroacetic* acid fails to undergo a simple pyrolysis into chloroform and carbon dioxide. Instead, it appears to decompose [33] in accordance with the following equation:

$$2CCl_3{-}CO_2H \longrightarrow CCl_3{-}COCl + CO_2 + CO + 2HCl.$$

This experiment was performed in a sealed tube at 300° for 4 hours. The gaseous products, by volume, are carbon dioxide 23.2 percent; carbon monoxide 25.4 percent; hydrogen chloride 51.4 percent. Possibly the reaction mechanism includes a bimolecular interchange of hydroxyl and one of the chlorines, giving trichloroacetyl chloride and $[HO{-}CCl_2{-}CO_2H]$, which should yield the gaseous products which were observed. It would be interesting to see if trichloroacetic acid would react with carbon tetrachloride under similar conditions to yield trichloroacetyl chloride, phosgene and hydrogen chloride. However, the decomposition of trichloroacetic acid into chloroform and carbon dioxide proceeds fairly well in hot aqueous solution, and especially well by warming in such basic solvents as aniline.

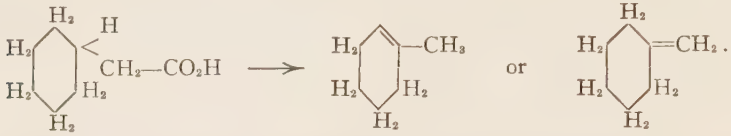
Boeseken has recently established [35] that pentachloro-propionic acid, $CCl_3{-}CCl_2{-}CO_2H$, decomposes in hot water into tetrachloro-ethylene, $CCl_2{=}CCl_2$, carbon dioxide, and hydrogen chloride.

α,γ-Dichlorobutyric acid, $CH_2Cl{-}CH_2CHCl{-}CO_2H$, yields [36] a chlorobutyro-lactone when it is dry distilled. The α-chlorine is inert in this case, relatively speaking. Similarly, δ-valerolactone [37] may be formed by the distillation of δ-chlorovaleric acid. Cloves [38] pointed out that a polymeric lactone was also produced here, and he recommended the use of δ-iodovaleric acid to avoid this. *Gamma* lactones were formed by heating the following acids [39] in water: β,γ-dibromobutyric acid, γ-bromocaproic acid and γ,δ-dibromovaleric acid. At 180-185°, γ-chloro-

[33] Engler and Steude, *Ber.* **26**, 1443 (1893).
[34] Grassi-Cristaldi, *Gazz. chim. ital.* **27**, II, 502 (1897).
[35] Boeseken, *Rec. trav. chim.* **46**, 841 (1927).
[36] Michael, *Ber.* **34**, 4053 (1901).
[37] Funk, *Ber.* **26**, 2574 (1893).
[38] Cloves, *Ann.* **319**, 357 (1901).
[39] Fichter and Sonneborn, *Ber.* **35**, 938 (1902); Messerschmidt, *Ann.* **208**, 101 (1881).

butyric acid [40] undergoes pyrolysis into butyrolacetone and hydrogen chloride.

Some acids which are related to acetic acid may eliminate carbon dioxide by heating, but the other substance is not the simple compound which would be expected. Thus, cyclohexyl-acetic acid [41] gives either methyl-1-cyclohexene-1,2 or methylene-cyclohexylidene; thus,

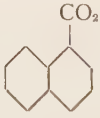


The former is produced by heating at 300° under pressure, and the latter by slow heating in an open vessel. In the case of di-(*p*-nitrophenoxy)-acetic acid, $(O_2N—C_6H_4—O—)_2CH—CO_2H$, only a little over half of the theoretical amount of carbon dioxide is eliminated [42] by long heating at 195-200°. The product of the reaction is chiefly *p*-nitrophenol.

Aromatic Acids.

Benzoic acid may be transformed [43] into benzene in 80 percent yields if it is heated in an aluminum apparatus at 500° in a current of steam. Steam augments the yield of benzene, and if lime or sodium hydroxide is present, the yield is stated to be 93 percent. The use of soda-lime to assist difficult decarboxylations is, of course, quite general.

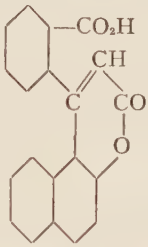
Meyer and Hofmann [44] reported a variety of products when benzoic acid is pyrogenically decomposed. These include benzene, benzaldehyde, diphenyl, *p*-phenyl-benzoic acid and a small quantity of 4,4′-dicarboxy-diphenyl. The tendency for two aromatic nuclei to condense with the elimination of hydrogen is one of the characteristic high-temperature effects which has already been noted (p. 93). Meyer and Hofmann considered that this hydrogen reacted with the original acid to form the benzaldehyde.

α-Naphthoic acid (melting point 157-160°), 

, recrystallized from glacial acetic acid, may be heated for two hours at a temperature of 295° with very little change. However, if it is heated [45]

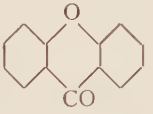
[40] Henry, *Compt. rend.* **101**, 1158 (1885).
[41] Zelinsky and Gutt, *J. Russ. Phys. Chem. Soc.* **37**, 1062 (1906); *Chem. Abstracts* **1**, 1397 (1907).
[42] Bischoff, *Ber.* **40**, 3170 (1907).
[43] Schrader and Wolter, *Ges. Abhandl. Kennt. Kohle* **6**, 79 (1921); *Chem. Abstracts* **19**, 48 (1924).
[44] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).
[45] Hurd and Smith, unpublished results.

under a reflux for 1.5 hours, only 0.034 mol from an original 0.058 may be recovered, and 0.01 mol of carbon dioxide is evolved. β,β-Dinaphthyl is formed also.

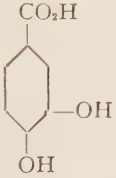
With 4-(2-carboxyphenyl)-5,6-benzocoumarin,  , there

is simple decarboxylation [46] to 4-phenyl-5,6-benzocoumarin by distillation (300-350°) at atmospheric pressure. The 3,4-dihydro derivative likewise loses its carbon dioxide on distillation, giving 4-phenyl-3,4-dihydro-5,6-benzocoumarin. In this case, the gas evolution starts at 260°.

p-Hydrazinobenzoic acid, $H_2N—NH—C_6H_4—CO_2H$, melts [47] between 220-225°, and decomposes in part into carbon dioxide and phenylhydrazine. Distillation [48] of phenyl-anthranilic acid induces an almost complete transformation into diphenylamine and carbon dioxide with the simultaneous formation of only traces of acridone. Triphenylamine-*o*-carboxylic acid decarboxylates itself quantitatively [49] into triphenylamine, if it is maintained at 200° for a short time. This is, in fact, the last step of a convenient synthesis of triphenylamine.

o-Phenoxy-benzoic acid [50] distils at 355° with a small amount of decomposition. The acid distillate contains some xanthone,  ,

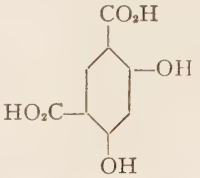
and this reaction may be made quantitative with sulfuric acid.

If protocatechuic acid,  $\cdot H_2O$, is heated [51] at 200°, or

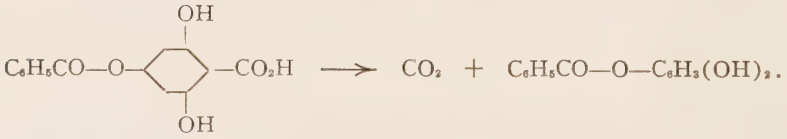
230° or 300° for one hour, first the water of crystallization is expelled and then carbon dioxide and catechol are formed. However, the calculated quantity of carbon dioxide is 25.58 percent, and the isolated quantities, respectively, are 5.46, 13.42 and 19.30 percent. Small amounts of

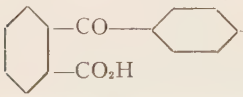
[46] Dischendorfer and Danziger, *Monatsh.* **48**, 332 (1927).
[47] Fischer, *Ann.* **212**, 338 (1882).
[48] Graebe and Lagodzinski, *Ann.* **276**, 44 (1893).
[49] Goldberg and Nimerovsky, *Ber.* **40**, 2448 (1907).
[50] Graebe, *Ber.* **21**, 503 (1888).
[51] Kunz-Krause and Manicke, *Ber.* **53**, 190 (1920).

tetrahydroxyanthraquinone (rufiopin) are also formed as a sublimation product if the acid is heated in a test tube in a direct flame. The carbon dioxide elimination from gallic acid is nearly quantitative after one hour's heating at 250°. Pyrogallol is the chief product, but here again, a little rufigallic acid (hexahydroxyanthraquinone) is also produced as a result of direct heating.

In the case of  , both carboxyls are lost at the melting point, 192°, and resorcinol [52] is formed. The bromo-dihydroxybenzoic acids are decarboxylated with comparative ease, but the corresponding ether,[53] 2,4-dimethoxy-5-bromobenzoic acid is not changed by three hours' boiling in xylene, nor by vacuum distillation, nor by heating to 360° with soda-lime *in vacuo* (but not undecomposed by heating at atmospheric pressure). The influence of the kind and place of substituents [54] upon the firmness of the union of the carboxyl group in substituted benzoic acids has been studied by von Hemmelmayr. In his work, the acids were heated with water or with aniline.

Benzoylphloroglucinol-carboxylic acid [55] undergoes pyrolysis in 20 minutes at 200° (oil bath temperature) into carbon dioxide and benzoylphloroglucinol:



The yield is 77 percent. Opianic acid behaves differently.[56] As a result of 4 hours' maintenance at 200° and then 2 hours at 230°, it gives opianic anhydride. Opianic acid possesses an *ortho* carbonyl group; it is 2,3-dimethoxy-6-aldehydo-benzoic acid. 2-*p*-Toluylbenzoic acid,  , is another substance which possesses a carbonyl group *ortho* to the carboxyl. Here also, dehydration [57] occurs

[52] Tiemann and Lewy, *Ber.* **10**, 2212 (1877).
[53] Rice, *J. Am. Chem. Soc.* **48**, 3126 (1926).
[54] von Hemmelmayr, *Monatsh.* **34**, 365 (1913).
[55] Fischer, *Ann.* **371**, 308 (1910).
[56] Fargher and Perkin, Jr., *J. Chem. Soc.* **119**, 1724 (1921).
[57] Limpricht and Wiegand, *Ann.* **311**, 184 (1900).

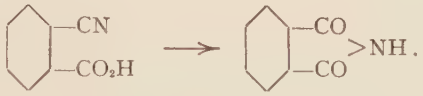
by heating. No change is apparent at 200°, but the compound is completely altered in 6 hours at 250-260°. Apparently there is a peculiar anhydride formation, represented by the following equation:

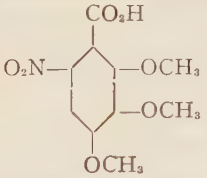
$$6C_{15}H_{12}O_2 \longrightarrow C_{90}H_{62}O_3 + 5H_2O,$$

and above 260° the following:

$$4C_{15}H_{12}O_2 \longrightarrow C_{60}H_{42}O_9 + 3H_2O.$$

An *o*-CN group also inhibits the elimination of carbon dioxide. For example, fusion at 187° of *o*-cyanobenzoic acid induces [58] a rearrangement into phthalimide:

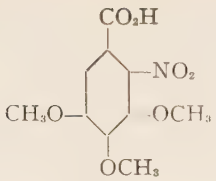


An accumulation of nitro groups favors the elimination of carbon dioxide. 2,4,6-Trinitrobenzoic acid changes [59] into trinitrobenzene by melting (melting point 210°), or by heating in water. The case of nitro-trimethyl-pyrogallol-carboxylic acid, 

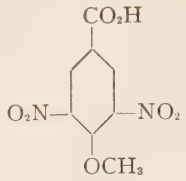
, is interesting because in spite of carbon dioxide elimination, which continues [60] for 1.5-2 hours at 170-190°, there is formed none of the anticipated trimethoxy-nitrobenzene. Instead, the two chief products of the reaction are the methyl ester of the original acid (1 gram from 3 grams of the acid), and the dimethyl ether, $C_6H_2(NO_2)(OCH_3)_2(OH)$, in a yield of 0.075 gram. This indicates the wandering of an alkyl group. Simple phenolic ethers (p. 201) undergo pyrolysis to phenols. The change of an OCH_3 group into an OH group is not out of harmony with this fact.

Later experiments [61] were performed in an effort to determine the effect of the nitro group and of the methoxyl groups in this pyrolysis. The following substances were distilled at atmospheric pressure and under diminished pressure: *o*, *m*, and *p*-methoxy-benzoic acids, and also the following:

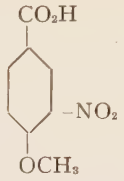
[58] Allendorff, *Ber.* **24**, 2348 (1891).
[59] D.R.P. 77,353; Frdl. IV, 34.
[60] Pollak and Goldstein, *Ann.* **351**, 161 (1907).
[61] Pollak and Feldscharek, *Monatsh.* **29**, 139 (1908).



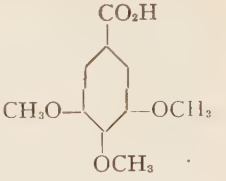
nitro-3,4,5-trimethoxybenzoic acid



dinitroanisic acid



nitroanisic acid



trimethyl ether of gallic acid

A summary of the results follows.

The presence of a nitro group in the molecule decreases the stability of the acid and favors the formation of the ester; thus, the first two compounds are largely transformed into their methyl esters by vacuum distillation.

An increase in the number of nitro groups is accompanied by a marked decrease in stability. For example, dinitroanisic acid is converted into its methyl ester by distillation at 12 mm., whereas nitroanisic acid is only partially converted into the ester at 40 mm.

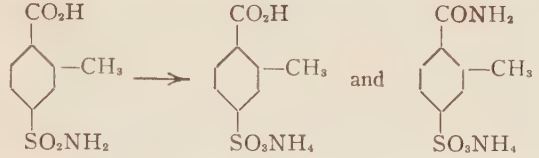
The methoxy acids which do not contain a nitro group may be distilled in a vacuum without undergoing pyrolysis, but decomposition may set in by distillation at ordinary pressure. When *o*-methoxybenzoic acid is distilled at ordinary pressure (200° or above), it changes into a mixture of methyl salicylate and methyl *o*-methoxybenzoate; there are also traces of phenol, but no anisole whatsoever. *m*-Methoxybenzoic acid is much more stable than the *o*-isomer, and anisic acid is between these two substances but it is also considerably more stable than the *o*-isomer. Both *m*- and *p*-methoxybenzoic acids, nevertheless, give their respective methyl esters if they are heated for several hours at 180-270°. Some anisole is formed in this manner from anisic acid.

Since the trimethyl ether of gallic acid pyrolyzes less readily than *o*-methoxybenzoic acid, it follows that the *o*-methoxyl has a greater influence on the instability of the compound than an accumulation of methoxyls in other positions. However, it is far less stable than anisic acid, or *m*-methoxybenzoic acid.

The sulfamido-benzoic or -toluic acids form another type of compounds whose pyrolysis is spectacular. When *p*-sulfamidobenzoic acid, $HO_2C—C_6H_4—SO_2NH_2$, is heated for some time near its melting point, 285°, it chars considerably but becomes partially converted into the ammonium salt of *p*-sulfobenzoic acid.[62] At higher temperatures,[63]

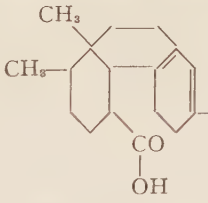
[62] Remsen, Hartman and Muckenfuss, *Am. Chem. J.* **18**, 150 (1896). Stoddard, Chamberlain, Waters, Nakesko, Rouiller, *ibid.* **47**, 1, 318, 333, 429, 475 (1912).
[63] Remsen and Muckenfuss, *ibid.* **18**, 349 (1896).

benzonitrile appears. Another curious result [64] of similar nature was reported by Nowell, who heated *p*-sulfamido-*o*-toluic acid at 220° for 2 hours. The mechanism is obscure, but acid ammonium sulfotoluate and ammonium 4-carbamido-3-methyl-benzenesulfonate are the isolated products:



In the cases listed in Table XXXVIII, there is simple decarboxylation by heating.

Various statements have appeared in the literature concerning the behavior of abietic acid towards heat. Knecht [65] reported that this material loses water somewhat below the melting point, but experiments by Ruzicka and by Shaw and Sebrell indicate [66] that this is not the case. In a vacuum of 0.3 mm., abietic acid distils unchanged (bath temperature 260°; vapors at 205°)

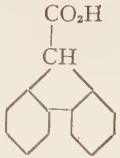
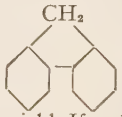
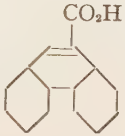
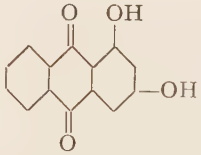
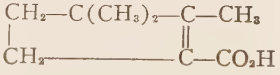
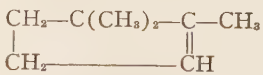
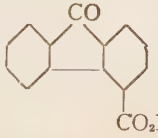
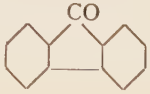


Abietic Acid ($C_{19}H_{29}$—CO_2H)

. By heating for 8 hours at 300° in a stream of hydrogen or carbon dioxide, there is only formed 0.28 mol of water, as compared with the 0.5 mol which would be required for anhydride formation. In addition, the gaseous products contain 0.21 mol of carbon dioxide, 0.06 mol of carbon monoxide, 0.05 mol of methane, and 0.02 mol of hydrogen. By fractionation of the residue, there is formed, according to Ruzicka and Schinz, about 60 percent of an unsaturated hydrocarbon oil, about 10 percent of an acid, and a residue which was considered to be decomposed abietic anhydride. Shaw and Sebrell reported that abietic acid gives no water on heating, but that it is readily oxidized to a monoxy derivative (even in a current of commercial carbon dioxide gas which invariably contains a little oxygen). It is this monoxy derivative which readily evolves water on heating at 180° to produce monoxyabietic anhydride. If abietic acid is heated in a current of *pure* carbon dioxide,

[64] Nowell, *Am. Chem. J.* **48**, 223 (1912).
[65] Knecht, *J. Soc. Dyers Colourists* **39**, 338 (1923).
[66] Ruzicka and Schinz, *Helv. Chim. Acta* **6**, 833 (1923); Ruzicka and Pfeiffer, *ibid.* **8**, 632 (1925); Shaw and Sebrell, *Ind. Eng. Chem.* **18**, 612 (1926).

TABLE XXXVIII. *Examples of Simple Decarboxylation by Heating.*

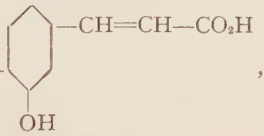
Original Acid	Conditions of Reaction	Product Formed	Reference
	280-290°	 Partial yield. If soda-lime is used, the carboxyl is completely removed.	Friedländer, *Ber.* **10**, 125 (1877).
	vacuum distillation	phenanthrene	Japp, *J. Chem. Soc.* **37**, 86 (1880).
$C_{14}H_5O_2(OH)_2—CO_2H$ (carboxyl in 2- or 4-)	at its melting point, 231°	 purpuroxanthin	Schünk and Roemer, *Ber.* **10**, 173 (1877).
 *β*-campholytic acid	4 hours, 300°, in tube	 "*iso*laurolene," quantitative yield	Blanc, *Ann. chim. phys.* [7] **18**, 215 (1899).
	450°	 fluorenone	Graebe and Aubin, *Ann.* **247**, 276 (1888).

no water is eliminated. With pinabietic acid, $C_{19}H_{29}CO_2H$, Aschan [67] reported the elimination of carbon monoxide and water and the production of pinabietin, $C_{19}H_{28}$, as the result of heating at ordinary pressure.

Unsaturated Acids.

Acids with α,β-Unsaturation.

Cinnamic acid decomposes gradually by slow distillation (300°) into styrene [68] and carbon dioxide. If heated rapidly, it may be distilled with but little decomposition. Freundler [69] reported a mixture of styrene and metastyrene as the result of 4 hours' heating of cinnamic acid in a sealed tube at 350°. As a preparative method for the synthesis of styrene, it has been found [70] that 1 kg. of crude cinnamic acid gives 360 grams of crude styrene, which, after being freed from metastyrene by vacuum distillation followed by fractionation at atmospheric pressure gives 320 grams (45.5 percent of theory) of pure styrene. In this preparation, a 4-liter copper retort was employed, and the heating was conducted during 4 to 5 hours with a low flame. Recent patents [71] have been granted for this preparation. Molten cinnamic acid is dropped into a chamber at 295-298° and the styrene which is formed is removed. Temperatures of 500-650° are also specified.

At 200°, caffeic acid,  , loses [72] carbon dioxide quantitatively, and leaves an amorphous brown residue, which by dry distillation or by vacuum distillation, gives good yields of catechol. Its monomethyl ether (3-hydroxy-4-methoxy-cinnamic acid) pyrolyzes [73] somewhat above its melting point (228°) into a body whose odor is said to be reminiscent of styrene and guaiacol.

The fact that cinnamic acid decomposes with so much more ease than hydrocinnamic acid points to the more negative character of the $C_6H_5CH{=}CH{-}$ group (see pp. 76, 337). Dinitrocinnamic acid, even at 0°, decomposes [71] into carbon dioxide and dinitrostyrene. The corresponding acids in the acetylene series also eliminate carbon dioxide with

[67] Aschan, *Ann.* **424**, 117 (1921).
[68] Howard, *Jahresbericht der Chemie* **1860**, 303.
[69] Freundler, *Compt. rend.* **124**, 1157 (1897); *Bull. soc. chim.* **17**, 613 (1897).
[70] Kraemer, Spilker and Eberhardt, *Ber.* **23**, 3269 (1890); Abbott and Johnson, *Organic Syntheses*, John Wiley and Sons, New York, Vol. 8, 84 (1928).
[71] Ostromislensky and Shepard, U. S. Pat. 1,541,176, Jan. 9, 1924; Ostromislensky, Can Pat., 261,326, June 1, 1926, *Chem. Abstracts* **20**, 424, 3461 (1926).
[72] Hlasiwetz, *Ann.* **142**, 227 (1867).
[73] Hoffmann, *Ber.* **9**, 686 (1876); Tiemann and Will, *Ber.* **14**, 955 (1881).
[74] Engler and Löw, *Ber.* **26**, 1441 (1893).

readiness. Thus, *phenyl propiolic acid*, $C_6H_5—C{\equiv}C—CO_2H$, at 120° (in water) gives phenyl acetylene; and *p*-nitrophenyl propiolic acid gives nitrophenyl acetylene at 100°. Aliphatic acetylene carboxylic acids pyrolyze with more or less ease to carbon dioxide. Distillation, but not vacuum distillation, will effect this transformation [75] with propiolic acid:

$$H—C{\equiv}C—CO_2H \longrightarrow C_2H_2 + CO_2.$$

Its homolog, $CH_3—C{\equiv}C—CO_2H$, boils at 203°, above which it gives allylene and carbon dioxide. The triple bond exerts little influence on the pyrolysis of unsaturated acids if it is not in the α,β-position.

β-Ethoxy-α-methyl-acrylic acid is almost quantitatively decomposed [76] by very slow heating into ethyl propenyl ether:

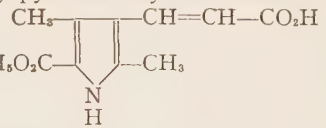
$$C_2H_5O—CH{=}C(CH_3)—CO_2H \longrightarrow CO_2 + C_2H_5—O—CH{=}CH—CH_3.$$

Since β-ethoxyacrylic acid is similarly converted into ethyl vinyl ether, this becomes a general method for the preparation of alkyl alkenyl ethers. Unsaturated thio-ethers [77] may be similarly prepared:

$$C_2H_5—S—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH—CO_2H \longrightarrow CO_2 + C_2H_5—S—\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

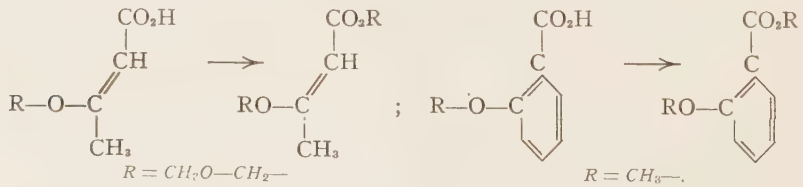
β-ethyl-thiocrotonic acid — *ethylthio-propylene*

Either of the two isomeric β-phenyl-Δ^{β}-hexenoic acids,[78] $\begin{matrix}C_6H_5\\ \\ C_3H_7\end{matrix}\!\!>\!C{=}CH—CO_2H$, lose carbon dioxide in the usual manner by dry distillation, yielding phenyl-pentene. A 70 percent yield [79] of 3-vinyl-2,4-dimethyl-5-carbethoxy-pyrrole may be realized by heating 1 gram portions of the acid,



, at 12-15 mm. up to 220°.

Methoxy-β-methoxy crotonic acid also loses carbon dioxide by distillation, but the acid becomes esterified in the process. Structurally, this acid bears a similarity to *o*-methoxybenzoic acid (p. 346), and the type of pyrolysis that each undergoes is similar.



$R = CH_3O—CH_2—$ $\qquad$ $R = CH_3—$.

[75] Baudrowski, *Ber.* **15**, 2701 (1882).
[76] Chichibabin, *J. prakt. Chem.* [2] **74**, 423 (1906).
[77] Autenrieth, *Ann.* **254**, 222 (1889).
[78] Johnson and Kon, *J. Chem. Soc.* **1926**, 2748.
[79] Fischer and Walach, *Ber.* **58**, 2818 (1925).

This reaction [80] has already been mentioned on p. 204. Presumably, acetone is also formed in the process.

Geranic acid also possesses α,β-unsaturation. Here again,[81] carbon dioxide is detached by distillation, and geraniolene is formed:

$$(CH_3)_2C{=}CHCH_2CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH{-}CO_2H \longrightarrow CO_2 + (CH_3)_2C{=}CHCH_2CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH_2.$$

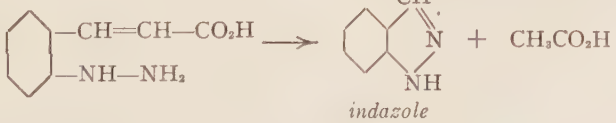
Decarboxylation of α,β-unsaturated acids is by no means the exclusive type of reaction induced by heat, but the presence of certain other groupings sometimes causes a totally different course for the pyrolysis. Aconitic acid illustrates this point. It contains not only the α,β-unsaturation, but also the succinic acid configuration. Therefore, if aconitic acid [82] is heated at 140° and 15-20 mm. for several minutes, aconitic anhydride remains as residue. This is a good method for its preparation.

$$HO_2C{-}CH{=}\underset{\displaystyle H_2C{-}CO{-}OH}{\overset{\displaystyle |}{C}}{-}CO{-}OH \longrightarrow HO_2C{-}CH{=}\underset{\displaystyle H_2C{-}CO}{\overset{\displaystyle |}{C}}{-}CO \quad >O + H_2O$$

The next immediate effect of heat is to change aconitic anhydride into itaconic anhydride. This is the simple decarboxylation reaction of the remaining carboxyl group, which possesses α,β-unsaturation. For a 63 percent yield the conditions were 15 mm. pressure and a bath temperature of 175-190°. Finally, itaconic anhydride undergoes isomerization into citraconic anhydride at a bath temperature of 250° and a pressure of 760 mm.:

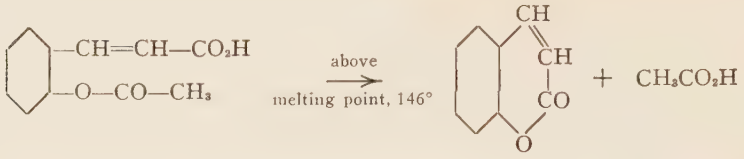
$$CH_2{=}\underset{\displaystyle H_2C{-}CO}{\overset{\displaystyle |}{C}}{-}CO \quad >O \longrightarrow CH_3{-}\underset{\displaystyle H_2C{-}CO}{\overset{\displaystyle \|}{C}}{-}CO \quad >O.$$

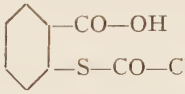
Maleanilic acid *o*-disulfide,[83] $(-S-C_6H_4-NH-COCH{=}CH-CO_2H)_2$, melts at 200°. Somewhat above that temperature, water is lost with the formation of a brown resin. *o*-Hydrazino-cinnamic acid [84] gives off acetic acid by heating, as does the acetyl derivative [85] of *o*-coumaric acid.



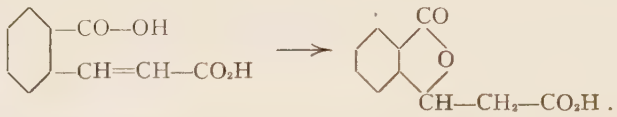
indazole

[80] Simonsen and Storey, *J. Chem. Soc.* **95**, 2106 (1909).
[81] Tiemann and Semmler, *Ber.* **26**, 2724 (1893).
[82] Anschütz and Bertram, *Ber.* **37**, 3968 (1904).
[83] Bogert and Stull, *J. Am. Chem. Soc.* **48**, 251 (1926).
[84] Fischer and Kuzel, *Ann.* **221**, 280 (1883).
[85] Tiemann and Herzfeld, *Ber.* **10**, 287 (1877).

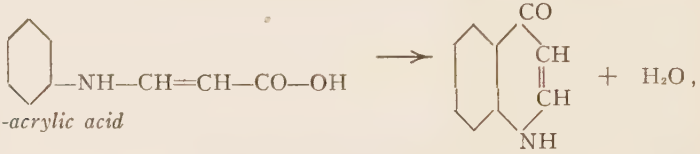


o-Coumaric acid, itself, splits out carbon dioxide at 200°, however (see p. 454). Acetic acid is also an observed product [86] of decomposition when acetyl thiosalicylic acid,  , is maintained above 125°.

Cinnamic *o*-carboxylic acid rearranges [87] at its melting point (183°) instead of pyrolyzing into simpler compounds:



The new compound melts at 147-150°. The following transformation:



has been described by Reissert,[88] but it has been pointed out that the heterocyclic formula of the compound which is produced is probably in error, since the substance is insoluble in acids, bases, and organic solvents.

Bromomethacrylic acid [89] or its geometric isomer may be distilled, but by 7-9 hours of refluxing, a charred residue remains. For the most part, however, there is pyrolysis according to the equation:

$$Br—CH=C(CH_3)—CO_2H \longrightarrow HBr + CO_2 + C_3H_4 .$$

The C_3H_4 represents allene, admixed with small amounts of methyl acetylene. To explain this, the following mechanism is suggested:

$$CHBr=C(CH_3)—CO_2H \xrightarrow{-CO_2} CHBr=CHCH_3 \xrightarrow{-HBr}$$

$$HC\equiv C—CH_3 \xleftarrow{+HBr} H_2C=CBr—CH_3 \xrightarrow{-HBr} H_2C=C=CH_2 .$$

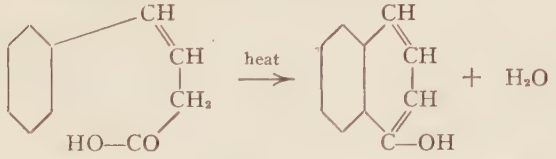
[86] Hinsberg, *Ber.* **43**, 654 (1910).
[87] Roth, *Ber.* **47**, 1597 (1914).
[88] Reissert, *Ber.* **20**, 3109 (1887); Meyer and Jacobson, "Lehrbuch der Organischen Chemie." Berlin and Leipzig, Walter de Gruyter Co., II, 3, 970.
[89] Lossen, Morschöck and Dorno, *Ann.* **342**, 166 (1905).

This is made plausible by the data [90] on the heating of the calcium salt; here, the hydrogen bromide becomes tied by the calcium ion, and the effluent gas is largely methyl acetylene, with only traces of allene.

In addition to the decomposition reactions of unsaturated acids, frequently also the conversion among geometric isomers may be accomplished by heat. Possibly the most familiar case is the conversion of fumaric acid into maleic anhydride. Above 100°, *iso*crotonic acid becomes partially changed [91] into crotonic acid. Angelic acid, $CH_3CH{=}C(CH_3){-}CO_2H$, may be changed into its isomer, tiglic acid,[92] either by long refluxing or by heating at 300° in a sealed tube. By heating also, allocinnamic acid is changed into cinnamic acid,[93] and a very analogous case is the change of *o*-cyano-allo-cinnamic acid,[94] $NC{-}C_6H_4{-}CH{=}CH{-}CO_2H$, into the higher melting *o*-cyanocinnamic acid (melting point 256°). The latter rearrangement is brought about by a few minutes' heating above the melting point (141°) of the allo-acid. The rearrangement of phenyl oleate into phenyl elaidate, although a transformation of an unsaturated ester [95] instead of an unsaturated acid, is similar.

Acids with β,γ-Unsaturation.

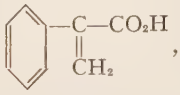
Fittig and Erdmann's synthesis [96] of α-naphthol from β-benzylidene-propionic acid is illustrative of β,γ-unsaturation.



In the glutaric series, carbon dioxide is eliminated [97] in the normal manner: $C_6H_5NH{-}CO{-}C(CH_3){=}CH{-}CH_2{-}CO_2H$, or α-methyl glutaconic-trans*semi*anilide, loses carbon dioxide at 195°; the α-ethyl compound, and the α-benzyl compound behave similarly at 180° and 190° respectively. α,α-Dimethyl-glutaconic acid, at 200°, changes into pyroterebic acid (see p. 415):

[90] Lossen, Morschöck and Dorno, *ibid.* p. 173.
[91] Hemilian, *Ann.* **174**, 330 (1874); Michael and Schulthess, *J. prakt. Chem.* [2] **46**, 252 (1892); Morrell and Hanson, *J. Chem. Soc.* **85**, 1520 (1904); Pomeranz, *Ann.* **351**, 354 (1907).
[92] Demarcay, *Ber.* **9**, 1933 (1876); Kopp, *Ann.* **195**, 90 (1879); Fittig, *Ann.* **259**, 6 (1890); **283**, 65, 107 (1894); Purdie and Marshall, *J. Chem. Soc.* **59**, 481 (1891).
[93] Liebermann, *Ber.* **23**. 149 (1890).
[94] Edwards, *J. Chem. Soc.* **1926**, 813.
[95] Skraup and Beng, *Ber.* **60**, **942** (1927).
[96] Fittig and Erdmann, *Ber.* **16**, 43 (1883); Erdmann, *Ann.* **227**, 242 (1885).
[97] Thole and Thorpe, *J. Chem. Soc.* **99**, 2231 (1911).

$$(CH_3)_2C(CO_2H)-CH=CH-CO_2H \longrightarrow CO_2 + (CH_3)_2C=CH-CH_2-CO_2H.$$

Atropic acid,  , polymerizes [98] to a dimer if it is kept at 140° for a long time. This dimer is a mixture of α- and β-*iso*atropic acid. Atropic acid possesses conjugate double bonds, so that polymerization might be anticipated. Acids in the sorbic series, $=C=C-C=C-CO_2H$, also polymerize easily by thermal means. Sorbic acid,[99] or ethyl sorbate, is converted into a viscid polymer if heated in a sealed tube at 250°. Cinnamenyl-acrylic acid behaves similarly, but it becomes partially decarboxylated as well.

For the conversion of a β,γ-unsaturated acid, such as pyroterebic acid, into an isomeric γ-lactone, see p. 368.

Aldehyde Acids and Ketonic Acids.

Acids with an α-Carbonyl Group.

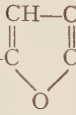
Glyoxylic Acid. If solid glyoxylic acid,[100] $C_2H_2O_3.H_2O$, is carefully heated, it is found to melt easily and then it appears to boil like water. The bubbles of gas condense in the cooler parts of the tube like steam. After a little time, the boiling nearly ceases; no distillate is formed, and only a few cc. of gas result from this process. The residue in the tube gels when cool. It is still water-soluble, but it has apparently undergone a reaction of the Cannizzaro type, since it contains oxalic and glycollic acids as well as unchanged glyoxylic acid.

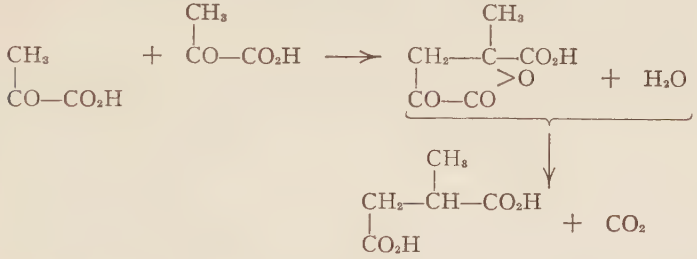
$$2\ CHO(CO_2H.H_2O) \longrightarrow CO_2H(CO_2H.H_2O) + CH_2OH(CO_2H)$$

If the slightly brown residue from the last experiment is heated at a higher temperature, carbon dioxide is evolved freely, and the residue becomes more glutinous and dark brown, but still there is no distillate. This time, the viscid residue (on cooling) is almost insoluble in water or alcohol. According to Debus, if the composition of one mol of carbon dioxide is deducted from the composition of one mol of glyoxylic acid, the elements of one mol of formaldehyde and one of water are left. These are considered to have formed the brown gelatinous residue.

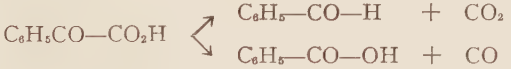
Pyruvic Acid, $CH_3-CO-CO_2H$. Prolonged heating of pyruvic

[98] Fittig and Wurster, *Ann.* **195**, 148 (1879).
[99] Doebner, *Ber.* **35**, 2129, 2538 (1902).
[100] Debus, *J. Chem. Soc.* **85**, 1391 (1904); *Ann.* **338**, 338 (1904).

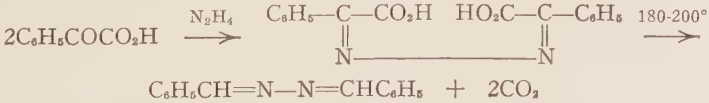
acid [101] at 170° gives acetic acid, carbon dioxide, α,α-dimethyl-furan-β-carboxylic acid,  , and some citraconic acid, $CH_3—C(CO_2H)=CH—CO_2H$. Wolff has shown that small yields (0.18 gram from 25 grams) of pyrotartaric acid (methyl succinic acid) are formed by 4 hours' refluxing of pyruvic acid. Much larger yields (2.4 grams from 9 grams) come by refluxing in the presence of concentrated hydrochloric acid. The following mechanism was proposed by Wolff:



Phenyl-glyoxylic Acid, $C_6H_5CO—CO_2H$. Both carbon dioxide and carbon monoxide are considered to be produced when phenyl glyoxylic acid [102] is distilled, for both benzaldehyde and benzoic acid are isolated products of the reaction. Some of the material



distils without change. In this work, no mention was made of an inert atmosphere, so that possibly the amount of benzoic acid which was obtained is not a true index to the amount of carbon monoxide which would also be produced. Claisen did not study the gaseous products of this pyrolysis. The fact that both benzaldehyde and benzoic acid are formed in this reaction was confirmed by Bouveault,[103] who stated, however, that most α-ketonic acids give good enough yields of aldehydes on pyrolysis to make it a satisfactory method of preparation. Bouveault devised an indirect pyrolytic method to pass from α-ketonic acids to aldehydes through the following steps:



[101] Völckel, *Ann.* **89**, 68 (1854); Böttinger, *Ann.* **188**, 303 (1877); *Ber.* **9**, 837 (1876); Wolff, *Ann.* **317**, 23 (1901).
[102] Claisen, *Ber.* **10**, 431, 1667 (1877).
[103] Bouveault, *Bull. soc. chim.* [3] **15**, 1015, 1018 (1896).

Hydrolysis of the benzaldazine gives benzaldehyde: see p. 646. The oxime of phenylglyoxylic acid also loses carbon dioxide by heating above its melting point; the other products are benzonitrile and water.

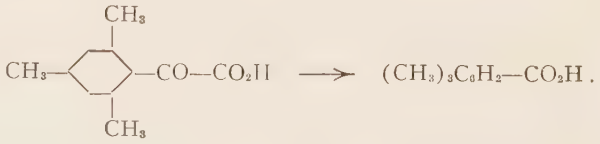
Unpublished results by F. E. Smith in the author's laboratory indicate that the carbon monoxide content in the gaseous portion from the pyrolysis of phenylglyoxylic acid (in an oil bath for 75 minutes at 200°) is not very large. An atmosphere of carbon dioxide was maintained throughout the experiment. This was removed by contact with a sodium hydroxide solution. In one run, the percentage yield of carbon monoxide found in this manner was 3.8 percent.

The chemical relationships of benzene and thiophene compounds are often very similar. It is of interest, therefore, to note that α-thienyl-glyoxylic acid [104] gives α-thienyl-formaldehyde by heating in an atmosphere of carbon dioxide. In this work, less than half of the theoretical yield is obtained, but even so it is the best method of preparation for this aldehyde:

There is some charring.

Phenyl-pyruvic Acid, $C_6H_5CH_2COCO_2H$, is stated [105] to yield carbon dioxide at its melting point (154°). Whether or not phenyl-acetaldehyde is also formed was not learned.

Other Glyoxylic Acids. When mesityl-glyoxylic acid [106] is dry distilled, the chief product of the reaction is said to be symmetrical trimethyl benzoic acid:

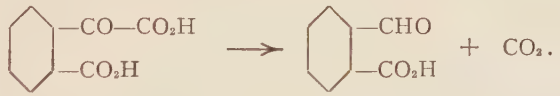


In the experimental conditions nothing was said about an inert atmosphere. Similarly, *o*-hydroxyphenyl-glyoxylic acid is reported to yield salicylic acid by distillation, and simultaneously much of the salicylic acid pyrolyzes [107] further into phenol and carbon dioxide. Xanthone was not mentioned by Schad, although it is known to be formed in the thermal decomposition of salicylic acid. Rather curiously, cymyl-

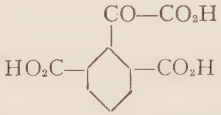
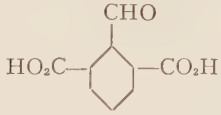
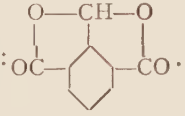
[104] Biedermann, *Ber.* **19**, 637 (1886).
[105] Plöchl, *Ber.* **16**, 2821 (1883); Wislicenus, *Ber.* **20**, 593 (1887).
[106] Meyer and Molz, *Ber.* **30**, 1276 (1897).
[107] Schad, *Ber.* **26**, 221 (1893).

glyoxylic acid gives a compound[108] by dry distillation which was thought by Bouveault to be 2,2′-dimethyl-5,5′-di*iso*propyl-benzophenone. However, Bert[109] has found that *p-iso*propyl-benzoic acid may be produced in very good yields from the corresponding α-keto acid. Starting with *iso*propyl bromide and benzene, cumene is synthesized by the Friedel and Crafts' reaction, which in turn is changed by the Friedel and Crafts' reaction into the ester, $(CH_3)_2CH—C_6H_4—CO—CO_2Et$, by reaction with ethoxalyl chloride. Hydrolysis of this ester to the acid, and pyrolysis of the acid gives $(CH_3)_2CH—C_6H_4—CO_2H$. The yield of the latter is 1100 grams from 1 kg. of commercial *iso*propyl bromide.

An observation[110] of Zincke and Breuer, and confirmed by Henriques, that *o*-carboxyphenyl-glyoxylic acid yields phthalic anhydride was supplemented by Graebe and Truempy. These investigators[111] found that if the acid was heated at 180°, that *o*-carboxybenzaldehyde (or its anhydride, dependent upon conditions) is formed. This is the normal course of a decarboxylation reaction:



Better yields (60-72 percent) of the aldehyde acid may be obtained if one does not heat the keto-acid directly, but proceeds through the bisulfite compound.

2,6-Dicarboxyphenyl-glyoxylic acid,[112]  , melts at 238° and at 240-260° it gives off carbon monoxide, carbon dioxide and water. Part of the yellow-colored residue is soluble in hot water, and part is not. The water soluble part contains *o*-carboxy-phthalic anhydride and 2,6-dicarboxy-benzaldehyde,  , whereas the insoluble portion contains an anhydride of the latter to which the following formula is assigned:  .

[108] Bouveault, *Bull. soc. chim.* [3] **17**, 942 (1897).
[109] Bert, *Bull. soc. chim.* **37**, 1397 (1925).
[110] Zincke and Breuer, *Ann.* **226**, 53 (1884); Henriques, *Ber.* **21**, 1610 (1888).
[111] Graebe and Truempy, *Ber* **31**, 370 (1898).
[112] Graebe and Bossel, *Ber.* **26**, 1797 (1893); *Ann.* **290**, 206 (1897).

β-Ketonic Acids.

The simplest β-aldehyde acid, [CHO—CH_2—CO_2H] or [CHOH=CH—CO_2H], has not been isolated. Attempts to prepare it give carbon dioxide and acetaldehyde instead. The aldehyde acid, [CHO—CHOH—CO_2H], is also unknown. However, the phenyl analog,[113] CHO—$CH(C_6H_5)$—CO_2H or its enol, is isolable.

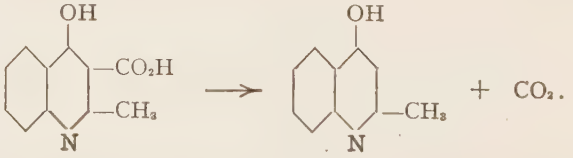
β-Ketonic acids in general undergo a very facile decomposition into carbon dioxide and a ketone. This is the basis for the well-known "ketone-splitting" of acetoacetic ester. The ester is hydrolyzed by a dilute acid to acetoacetic acid, which then decomposes into acetone. Homologs behave similarly. *Acetoacetic acid* may be isolated if care is exercised. It is a hygroscopic sirup which breaks down stormily into acetone and carbon dioxide below 100°. The dimethyl homolog, $CH_3COC(CH_3)_2CO_2H$, may be isolated as crystals; these, however, continually [114] evolve carbon dioxide and methyl*iso*propyl ketone.

Two interesting cases are γ,γ,γ-trimethylacetoacetic acid and benzoylacetic acid. In both cases, a tertiary carbon is linked to the carbonyl group. Crystals of the former, $(CH_3)_3C$—CO—CH_2—CO_2H, melt at 47-49° without visible gas evolution, but pyrolysis [115] into pinacolone occurs below 100°. Crystals of benzoylacetic acid, $C_6H_5COCH_2CO_2H$, melt at 103-104° with decomposition into acetophenone. The phenyl derivative, desyl formic acid, $C_6H_5COCH(C_6H_5)$—CO_2H, is unstable [116] and changes at once into carbon dioxide and desoxybenzoin.

Bis-(carboxydiphenoxymalonyl) urea [117] loses its two carboxyl groups by fusion. In spite of a rather complex molecule, the reaction is one of the normal type for β-ketonic acids:

$$CO(NHCOC(OC_6H_5)_2—CO_2H)_2 \longrightarrow 2CO_2 + CO(NHCOC(OC_6H_5)_2—H)_2.$$

An example of a β-ketonic acid, or rather of its enol isomer, in which the functional group is part of a heterocyclic nucleus, is 2-methyl-4-hydroxyquinoline-3-carboxylic acid. This melts [118] with decomposition at 245°, and produces 2-methyl-4-hydroxyquinoline:



[113] Wislicenus, *Ber.* **20**, 2931 (1887).
[114] Ceresole, *Ber.* **15**, 1874 (1882); Otto, *Ber.* **21**, 93 (1888); Moureu and Delange, *Bull. soc. chim.* **29**, 666 (1903); Bouveault and Locquin, *ibid.* **31**, 1153 (1904); Wahlberg, *Ber.* **44**, 2073 (1911).
[115] Baeyer and Perkin, J., *Ber.* **16**, 2129 (1883); Perkin, Jr., *J. Chem. Soc.* **45**, 170 (1884); Leighton, *Am. Chem. J.* **20**, 138 (1898).
[116] Beckmann and Paul, *Ann.* **266**, 20 (1891).
[117] van Praayle, *Rec. trav. chim.* **34**, 326 (1915).
[118] Overmyer, *J. Am. Chem. Soc.* **48**, 455 (1926).

The *N*-oxide, methylhydroxyquinoline carboxylic acid oxide, decomposes similarly into 4-hydroxyquinaldine oxide at its melting point (214°). Quantities of 1-1.5 grams were recommended for this preparation. The preparation of cyclopropyl methyl ketone [119] also follows the method of thermal decomposition of a β-ketonic acid:

$$\begin{matrix} CH_2 & COCH_3 \\ | & >C< \\ CH_2 & CO_2H \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} >CH—COCH_3 + CO_2.$$

Benzoylpyruvic acid, $C_6H_5COCH_2COCO_2H$, is not a β-keto acid, but is an α,γ-diketo acid. If, however, it decomposes in the manner of an α-keto acid, then either $C_6H_5CO—CH_2—CO_2H$ or $C_6H_5CO—CH_2—CHO$ should result by loss, respectively, of carbon monoxide or carbon dioxide. The β-carbonyl group of these substances would impart instability to the molecule, and acetophenone should be the ultimate product. It is found [120] in fact that carbon monoxide, carbon dioxide (80 percent of theory), and acetophenone.

γ- AND δ-KETONIC ACIDS.

Acids of this type are stable, and the simpler ones may be distilled in a vacuum. Distillation at atmospheric pressure, however, or distillation of the more complex and higher boiling compounds even under diminished pressure, causes dehydration of the molecule, thereby forming a 5- or a 6-membered ring. To illustrate: [121] during a slow distillation, the isomeric angelic lactones are formed from levulinic acid:

$$CH_3COCH_2CH_2CO_2H \longrightarrow H_2O + \begin{matrix} CH_3—C & = & CH—CH_2. \\ | & & | \\ O & —— & CO \end{matrix}$$

Exactly this type of pyrolysis has also been observed with:

α-methyl levulinic acid,	$CH_3COCH_2CH(CH_3)—CO_2H$
α-ethyl levulinic acid,	$CH_3COCH_2CH(C_2H_5)—CO_2H$
β-methyl levulinic acid,	$CH_3COCH(CH_3)—CH_2CO_2H$
α,β-dimethyl levulinic acid,	$CH_3CO—CH(CH_3)—CH(CH_3)—CO_2H$
α,α-dimethyl levulinic acid,	$CH_3COCH_2C(CH_3)_2CO_2H$
β-benzoyl propionic acid,	$C_6H_5COCH_2CH_2CO_2H$
benzyl levulinic acid,	$CH_3COCH(C_7H_7)CH_2CO_2H$
γ-acetyl butyric acid,	$CH_3COCH_2CH_2CH_2—CO_2H$
β,β-dimethyl-γ-acetyl butyric acid,	$CH_3COCH_2C(CH_3)_2—CH_2CO_2H$.

In a study of the conditions for ring formation by the pyrolysis of ketonic acids, Windaus and Bohne [122] observed the following regularities, and according to them there are no known exceptions. As will

[119] Perkin, Jr., *Ber.* **17**, 1441 (1884).

[120] Wislicenus, *Ber.* **28**, 813 (1895); *see also* Claisen and Brömme, *Ber.* **21**, 1133 (1888) who noticed carbon dioxide as a decomposition product, and also an oil which was thought to be benzoyl acetaldehyde but which undoubtedly was acetophenone.

[121] Wolff, *Ann.* **229**, 250 (1885); Pauly, Gilmour and Will, *Ann.* **403**, 151 (1914).

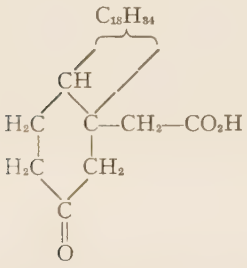
[122] Windaus and Bohne, *Ann.* **442**, 7 (1925).

be noticed subsequently, there are a few exceptional cases, but these are all caused by the presence of other functional groups. This reaction, therefore, provides a useful tool in the proof of structure.

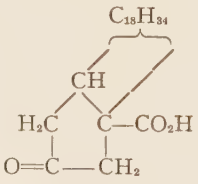
(1) The keto group must be *gamma* or *delta* to the carboxyl.
(2) A hydrogen atom must be held by the carbon atom which is adjacent to the keto group.

(3) If the functional group, $=CO-CH-\underset{|}{\overset{|}{C}}-CO_2H$, exists as part of a ring, the carboxyl-containing side-chain must be attached to a ring-carbon atom which is adjacent to the carbonyl group.

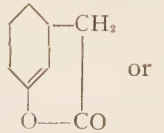
Two cyclic ketonic acids, related to cholesterol,



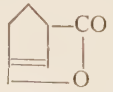
and



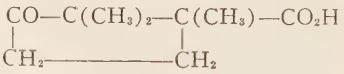
distil undecomposed *in vacuo*. Although these are *delta* and *gamma* ketonic acids, respectively, the side chain that holds the carboxyl is not attached to the *alpha* ring-carbon atom. The inability of these compounds to form the cyclic lactone is in conformity to the third generalization above, and it also agrees with Bredt's rule (p. 12), which stipulates that ring structures such as



or

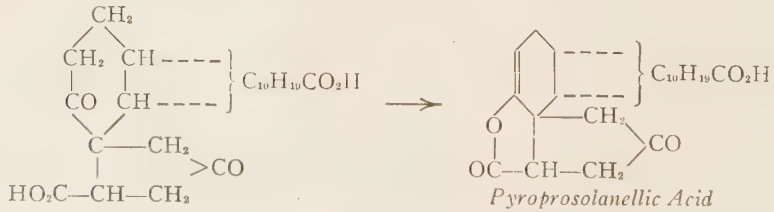


are impossible. Similarly, camphoronic acid,

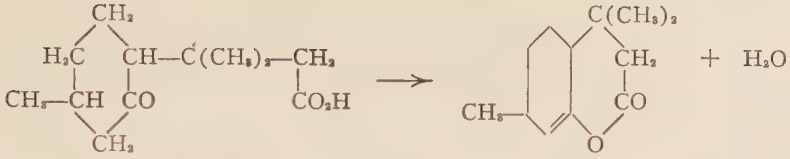


sublimes without decomposition.

Cyclic lactones are always formed, however, when the acidic side-chain is α- to the carbonyl group. The following cases have been developed, and are mentioned by Windaus and Bohne.

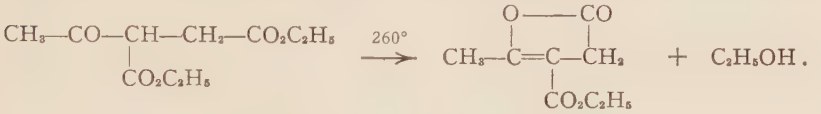


Pyroprosolanellic Acid

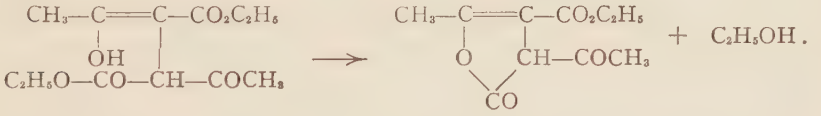


Pulegon-acetic Acid *lactone*

This type of pyrolysis is not limited to ketonic acids, but in certain cases γ-ketonic esters also undergo lactone formation with the elimination of alcohol. This is illustrated [123] with diethyl acetylsuccinate:

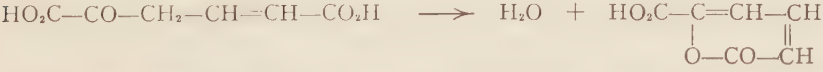


There is a similar reaction with the α-methyl, the α-ethyl and the α-propyl homologs. Diethyl diacetylsuccinate, $(CH_3COCHCO_2C_2H_5)_2$, that versatile compound which is theoretically capable of existing in at least 13 different isomeric forms, seemingly possesses an enolic structure as it is smoothly lactonized [124] by heat:



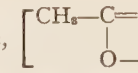
It is worth noting that both of the above esters are not only γ-ketonic esters but also β-ketonic esters. Thus, whereas the β-ketonic acids are much less stable than the *gamma*, this order of stability for the esters is reversed.

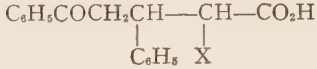
δ-Ketonic acids which possess α,β-unsaturation behave in the normal manner. Witness, for example, γ-oxalocrotonic acid [125] which becomes dehydrated to cumalin-carboxylic acid-(6) by melting it (190°):



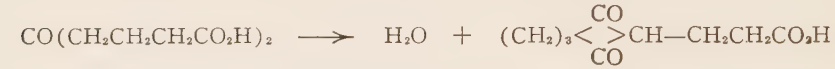
Should the unsaturation in *gamma* or *delta*-ketonic acids chance to be *beta-gamma*, then dehydration is not observed. β-Acetyl-acrylic acid is such an acid, and it becomes decarboxylated by distillation [126] at atmospheric pressure:

[123] Sprankling, *J. Chem. Soc.* **71**, 1159 (1897).
[124] Knorr, *Ann.* **293**, 92 (1896).
[125] Lapworth, *J. Chem. Soc.* **79**, 1280 (1901).
[126] D.R.P. 242,612; *Chem. Zentr.* **1912**, I, 385.

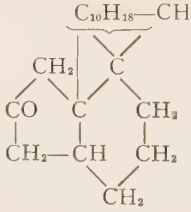
It is significant to note that a cyclic lactone,  , related to allene, would have been formed had the latter reaction pursued the normal course.

The δ-ketonic acids,[127]  , wherein $X =$ CN, or CO_2CH_3, are reported to lose carbon dioxide at 200°. The "malonic acid type" of pyrolysis in this case overbalances the δ-ketonic acid type.

A rather unusual case[128] is that of δ-ketoazelaic acid. The lactone, or the dilactone, which might be anticipated seems not to be formed. Water is eliminated by distillation, but the cyclic compound produced is dihydroresorcyl-propionic acid. Instead of a lactone nucleus, the nucleus is related to cyclohexane-dione.



This experiment was performed by heating the acid in 5-8 gram portions for a few minutes at its boiling point, 320°, and then distilling at 200 mm. with a yield of about 60 percent. This behavior is all the more extraordinary, because of the normal behavior of the tetramethyl homolog, $CO(CH_2—C(CH_3)_2—CH_2—CO_2H)_2$, which gives[129] a δ-dilactone on distillation with acetic anhydride.

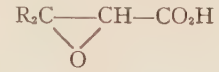
7-Ketocholanic acid is a keto acid[130] whose structure is partially determined, and is considered to be 

At 320-330°, it gives a 50 percent yield of a hydrocarbon, $C_{23}H_{36}$.

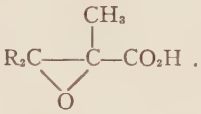
[127] Kohler, Graustein and Merrill, *J. Am. Chem. Soc.* **44**, 2536 (1922).
[128] von Pechmann and Sidgwick, *Ber.* **37**, 3823 (1904).
[129] Vorländer and Gartner, *Ann.* **304**, 8 (1899).
[130] Wieland and Schlichting, *Z. physiol. Chem.* **150**, 267 (1925).

O-Heterocyclic Acids.

Glycid Carboxylic Acids of the Type



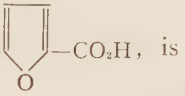
AND



Acids of this type [131] become decarboxylated by heating, and the resulting compounds are aldehydes or ketones, $R_2CH—CHO$ and $R_2CH—CO—CH_3$. Sometimes this behavior is noticed in the cold, and in other cases by vacuum distillation or by heating with water.

Furan Derivatives. A method has been developed by Wilson [132] by which furan is prepared in 72-78 percent yields from furoic acid without the use of sealed tubes:

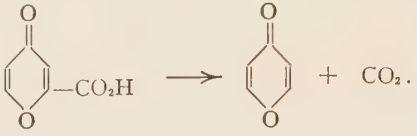
The acid is merely heated to 220° and the furan vapors are removed [133] at least 6 inches above the level of the acid. This method has been developed on a small plant scale. Older directions [134] recommended that furoic acid be heated for two hours in a sealed tube at 260-275°.

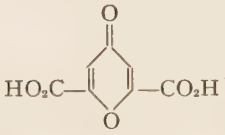
If furan-α,α'-dicarboxylic acid,  , is heated [135] in a free flame, furoic acid is formed by the loss of one of the two carboxyls. The yield is poor, as would be expected, because of the further pyrolysis of furoic acid into furan. If 2-furylfuran-3-carboxylic acid is pyrolyzed (melting point 177°), the products [136] are carbon dioxide and α,α'-difuryl. Similarly, 2-phenylfuran-3-carboxylic acid yields 2-phenylfuran, and 2-phenylpyrrole-3-carboxylic acid decomposes at 192° to yield 2-phenyl-pyrrole.

γ-Pyrane is unknown; Blaise and Gault [137] demonstrated that it

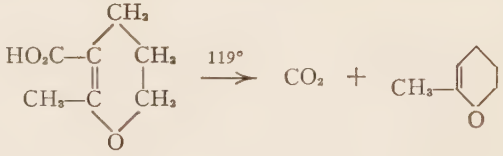
[131] Darzens, *Compt. rend.* **139**, 1214 (1904); **141**, 766 (1905). D.R.P. 174,239; 174,279; *Chem. Zentr.* **1906**, II, 1297-8.
[132] W. Courtney Wilson, "Organic Syntheses," Vol. VII, New York, John Wiley and Sons, **1927**, p. 40.
[133] Wilson, U. S. Pat. 1,636,030; *Chem. Abstracts* **21**, 2907 (1827).
[134] P. Freundler, *Compt. rend.* **124**, 1157 (1897); *Bull. soc. chim.* [3] **17**, 613 (1897).
[135] Sohst and Tollens, *Ann.* **245**, 21 (1888).
[136] Kondo and Suzuki, *J. Pharm. Soc. Japan*, No. **544**, 501 (1927); *Chem. Abstracts* **21**, 3362 (1927).
[137] Blaise and Gault, *Bull. soc. chim.* [4], **1**, 129 (1907).

could not be isolated in the thermal decomposition of γ-pyrane-α,α'-dicarboxylic acid. γ-Pyrone, however, may be prepared [138] from comanic acid by melting the acid (250°):

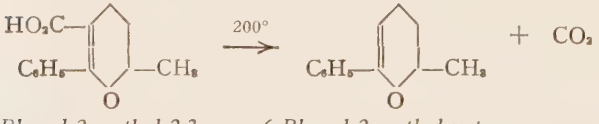


Chelidonic acid,  , chars considerably and undergoes pyrolysis [139] into a mixture of comanic acid and γ-pyrone. Willstätter and Pummerer [140] found that the decomposition into pyrone was greatly aided by the presence of copper powder, and obtained a 75 percent yield (crude) of pyrone. The partial decomposition of chelidonic acid into comanic acid is favored by heating the former in a vacuum.

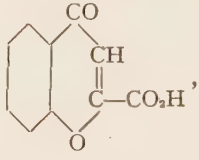
The following derivatives of dihydropyrane-carboxylic acid lose carbon dioxide at high temperatures, with the formation of dihydropyranes:



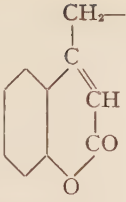
6-Methyl-2,3-dihydro-1,4-pyrane-5-carboxylic acid [141] — *"Anhydride of Aceto-butyl Alcohol"*



6-Phenyl-2-methyl-2,3-dihydro-1,4-pyrane-5-carboxylic acid [142] — *6-Phenyl-2-methyl-γ-pyrane-dihydride-2,3*

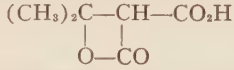
Chromone carboxylic acid,  , is converted [143] into

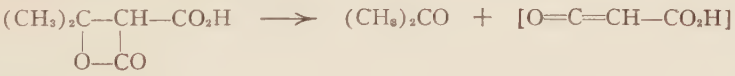
[138] Ost, *J. prakt. Chem.* [2] **29**, 61 (1884).
[139] Haitinger and Lieben, *Monatsh.* **6**, 279 (1885).
[140] Willstätter and Pummerer, *Ber.* **37**, 3745 (1904).
[141] Perkin, Jr., *Ber.* **19**, 2557 (1886); *J. Chem. Soc.* **51**, 702 (1887).
[142] Fargher and Perkin, *J. Chem. Soc.* **105**, 1363 (1914); this reference also lists other similar cases.
[143] Ruhemann and Stapleton, *J. Chem. Soc.* **77**, 1185 (1900).

chromone by distillation, and coumaryl-4-acetic acid,  , changes [144] into 4-methyl-coumarin at the melting point, 170°.

Lactonic Acids.

β-Lactonic Acids.

Carboxyl and Carbonyl Attached to the Same Carbon. The compounds of this type which have been investigated are the β-lactones of β-hydroxy*iso*propylmalonic acid,  , and its α-methyl homolog. With the former, Meldrum [145] reported a melting point of 97°, above which temperature carbon dioxide is evolved, the gaseous evolution becoming rapid at 130°. Ott,[146] however, showed that simple fission of carbon dioxide was quite inadequate, inasmuch as he showed a total absence of dimethylacrylic acid, $(CH_3)_2C{=}CH{-}CO_2H$, and the presence of 86 percent yield of acetone. Ott suggested the following primary pyrolysis:



to be followed by:

The isolation of a small amount of carbon suboxide tended to confirm this mechanism, and the low yield was explained on the basis of the reaction of carbon suboxide with water to form malonic acid (not isolated), and the subsequent decomposition of this to carbon dioxide and acetic acid, both of which were isolated. If the ketene-carboxylic acid decomposed entirely in this manner, some of the malonic acid should have escaped decomposition for this is stable up to 140°. Furthermore, only half of the carbon suboxide should have been taken from the reaction in this manner, since *one* mol of it needs *two* of water to produce malonic acid. It seems fully warranted to assume a concurrent pyrolysis of the hypothetical ketene carboxylic acid into

[144] Limaye *Quart. J. Indian. Chem. Soc.* **4**, 159 (1927); *Chem. Abstracts* **21**, 3193 (1927).
[145] Meldrum, *J. Chem. Soc.* **93**, 598 (1908).
[146] Ott, *Ann.* **401**, 159 (1914).

ketene and carbon dioxide. Ketene is known to accept water readily to form acetic acid. Thus:

$$[O{=}C{=}CH{-}CO_2H] \longrightarrow CO_2 + CH_2{=}C{=}O \xrightarrow{H_2O} CH_3CO_2H.$$

The homolog, α-methyl-β-hydroxy-*iso*propylmalonic acid lactone, was found to decompose at 110-113° into acetone (80-85 percent yield), an unidentified oil, and some carbon suboxide. It was not possible to demonstrate the presence of methyl ketene, but this may very well be due to the great reactivity of methyl ketene. In the first place, methyl ketene has never been isolated [147] except in a dilute ether solution. Secondly, if formed, it would undoubtedly have reacted with the methanol, which seems essential to explain the carbon suboxide, to form methyl propionate. Therefore, were methyl ketene carboxylic acid a transitory intermediate product, it would probably have had two concurrent reactions of pyrolysis:

$$\left[OC{=}C{<}\begin{matrix}CO_2H\\CH_3\end{matrix}\right] \begin{matrix}\nearrow\\\searrow\end{matrix} \begin{matrix}OC{=}C{=}CO + CH_3OH\\CO_2 + [CH_3CH{=}CO] \xrightarrow{CH_3OH} CH_3CH_2CO_2CH_3.\end{matrix}$$

Part of the methanol should also react with the carbon suboxide to form dimethyl malonate.

α-Bromo-β-hydroxy-*iso*propylmalonic acid lactone, a related compound, decomposes at 130° into acetone, carbon dioxide and hydrogen bromide. Carbon suboxide and hypobromous acid were not mentioned.

The methyl ester of α-methyl-β-hydroxy-*iso*propylmalonic acid lactone was found to decompose in about 25 percent amounts by slow distillation (213°). This is particularly interesting inasmuch as dimethyl ketene is formed thereby in 50 percent yields, based on the amount converted (hydrogen atmosphere).

$$(CH_3)_2C(O{-}CO){-}C(CH_3){-}CO_2CH_3 \longrightarrow (CH_3)_2CO + CO_2 + (CH_3)_2C{=}CO$$

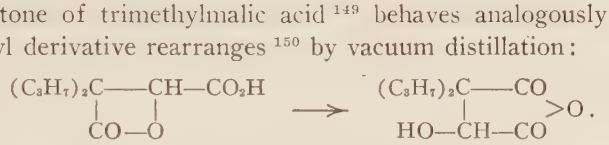
Similarly, by vacuum distillation, methyl-bromo-ketene was formed from the corresponding α-bromo ester. There is no literature record dealing with similar experiments on the lactonic ester, $(CH_3)_2C(O{-}CO){-}CH{-}CO_2CH_3$, which has an unsubstituted α-hydrogen. If such a compound behaved analogously, it would be expected to pyrolyze into methyl ketene.

Carboxyl and Oxygen Attached to the Same Carbon. It is characteristic of these β-lactones of the malic acid type to rearrange into the corresponding malic anhydride by distillation. The product of

[147] *See* p. 253 for the attempted synthesis of methyl ketene by the pyrolysis of diethyl ketone

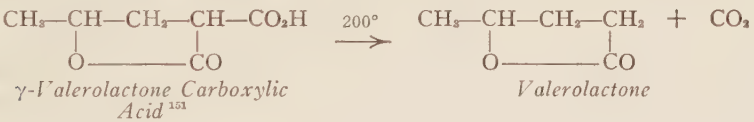
the rearrangement [148] in the case of the dimethyl derivative distils at 250-260° without loss of carbon dioxide:

The β-lactone of trimethylmalic acid [149] behaves analogously, and the di-*n*-propyl derivative rearranges [150] by vacuum distillation:

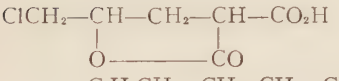


γ-Lactonic Acids.

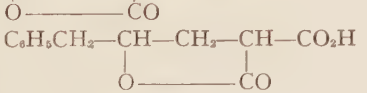
Carboxyl Attached to the α-Carbon. Acids of this type are structurally related to malonic acid, since they are lactones of γ-hydroxymalonic acids. Just as malonic acid loses one of its carboxyl groups easily by heating, so also the pyrolysis of these lactonic acids is merely one of decarboxylation. To illustrate:



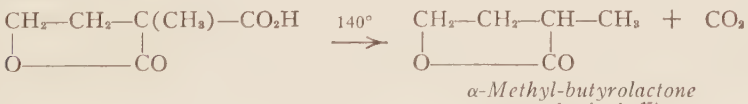
γ-Valerolactone Carboxylic Acid [151]



is decarboxylated [152] by heating *in vacuo*.



is decarboxylated [153] by vacuum heating at 130-140°.



α-Methyl-butyrolactone quantitatively [154]

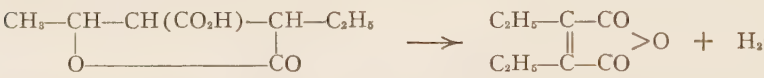
The Paraconic Acids; Carboxyl Attached to the β-Carbon Atom. Three concurrent reactions seem to enter in the pyrolysis of these compounds: *First,* and most important, is the formation of unsaturated acids with (and less frequently without) the loss of carbon dioxide. *Secondly,* the formation of a γ-lactone, with loss of carbon dioxide. There is reason to believe that these lactones are formed by

[148] Baeyer and Villiger, *Ber.* **30**, 1954 (1897); Fichter and Hirsch, *Ber.* **33**, 3270 (1900).
[149] Kommpa, *Ber.* **35**, 534 (1902).
[150] Bains and Thorpe, *J. Chem. Soc.* **123**, 2742 (1923).
[151] Fittig and Hjelt, *Ann.* **216**, 56 (1883).
[152] Leuchs and Splettstoesser, *Ber.* **40**, 301 (1907).
[153] von Auwers and Müller, *Ann.* **434**, 165 (1923).
[154] Marburg, *Ann.* **294**, 122 (1896); *Ber.* **28**, 10 (1895).

rearrangement of the aforementioned unsaturated acids, although it is convenient to look upon their formation as a simple decarboxylation. *Finally,* the formation of derivatives of maleic anhydride by loss of water. These three cases shall be presented in reverse order.

Maleic Anhydride Type. About one-fifth of α-methyl paraconic acid is converted [155] into dimethyl maleic anhydride (pyrocinchonic anhydride) by distillation at ordinary pressure. Some of the acid also distils unchanged.

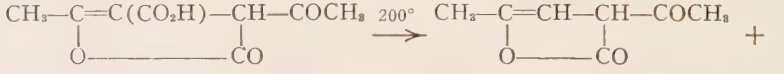
α-Ethyl-γ-methyl paraconic acid [156] also becomes partially transformed into diethyl maleic anhydride (xeronic anhydride) by similar means:



To a small extent, terebic acid (below) also behaves in this manner.

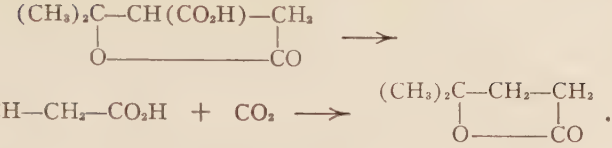
Decarboxylation to the γ-Lactone. By distillation, γ-methyl-paraconic acid is partially rearranged [157] into ethylidene succinic acid, $CH_3—CH=C(CO_2H)—CH_2—CO_2H$, and partially changed into γ-valerolactone:

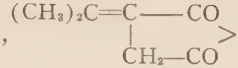
One mol of carbon dioxide is also removed from the unsaturated compound, *iso*carbopyrotritaric acid, and acetoangelicolactone is formed: [158]

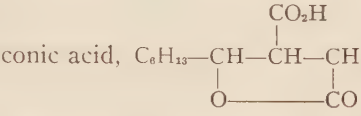


The variety of changes that terebic acid undergoes at its boiling point (207°) makes this compound one of unusual interest. A mixture of pyroterebic acid and γ-*iso*caprolactone result, and by refluxing the quantity of the latter may be made to increase at the expense of its isomer. Very good yields of the lactone [159] may be realized in this manner. The mechanism for the change may be represented as follows:

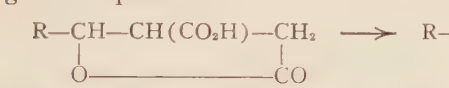
[155] Fichter and Rudin, *Ber.* **37**, 1610 (1904).
[156] Fichter and Obladen, *Ber.* **42**, 4703 (1909).
[157] Fittig, *Ann.* **255**, 10 (1889); Fittig and Weil, *Ann.* **283**, 279 (1894).
[158] Knorr, *Ber.* **22**, 165 (1889).
[159] Chautard, *J.* **1855**, 652; Williams *Ber.* **6**, 1095 (1873); Mielck, *Ann.* **180**, 52 (1876); Fittig and Bredt, *Ann.* **200**, 58 and 259 (1880); Bredt, *ibid.* **208**, 55 (1880); Koenigs and Hoerlin, *Ber.* **26**, 2048 (1893).



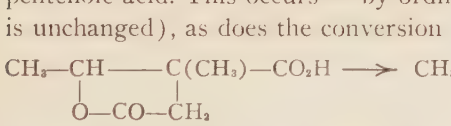
The formation of pyroterebic acid is in accordance with the general reaction given immediately below. A small isolated quantity of teraconic anhydride,  , is evidence of the other concurrent reaction.

If hexyl-paraconic acid,  , is gradually heated [160] to 300°, it gives the lactone of hexylbutyric acid in rather poor yields; decylenic acid, C_9H_{17}—CO_2H, is concurrently formed.

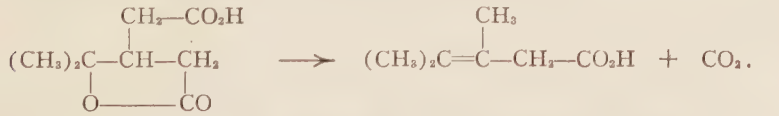
Formation of β-Unsaturated Acids. For this type of reaction, the general equation is:



α-Ethyl-γ-methyl-paraconic acid yields some diethyl-maleic anhydride as has been mentioned, but it yields still larger amounts of α-ethyl-β,γ-pentenoic acid. This occurs [161] by ordinary distillation (about 10 percent is unchanged), as does the conversion of β,γ-dimethyl paraconic acid:

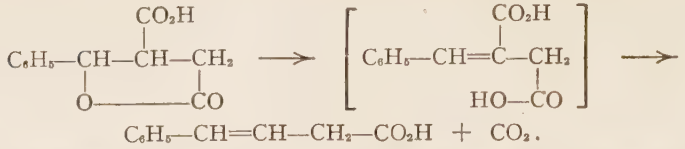


Terpenylic acid, with the carboxyl on a side chain, also pyrolyzes [162] in this manner and yields teracrylic acid by distillation:



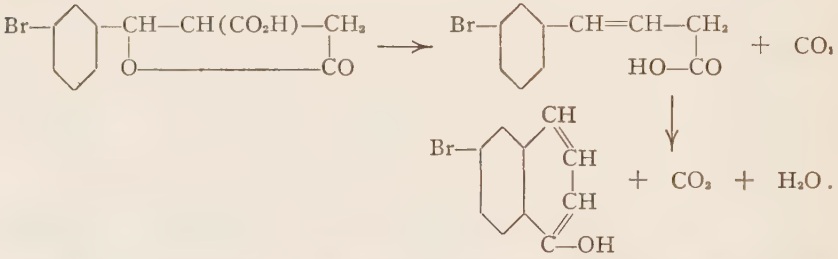
Phenyl paraconic acid, which may be formed in good yield from benzaldehyde, sodium succinate and acetic anhydride by Perkin's reaction, is converted into benzylidene propionic acid by distillation. Possibly this proceeds [163] through phenyl-itaconic acid, as an intermediate step.

[160] Fittig, *Ann.* **227**, 89 (1885).
[161] Fichter and Gisiger, *Ber.* **42**, 4708 (1909).
[162] Fittig and Krafft, *Ann.* **208**, 79 (1881).
[163] Jayne, *Ann.* **216**, 113 (1882); Erdmann, *Ann.* **227**, 258 (1885).



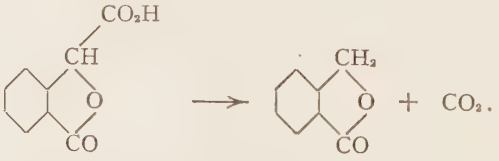
$$C_6H_5{-}CH{=}CH{-}CH_2{-}CO_2H + CO_2.$$

o-Chlorophenyl paraconic acid [164] and *o,m,* and *p*-bromophenylparaconic acids [165] have been found to give the same general reaction, the temperature of the pyrolysis in the case of the bromo-compounds being between 250-300°. In all of these cases, however, there is a further reaction which consists in the dehydration of the unsaturated acid to a derivative of α-naphthol. This would be anticipated, however, because of Erdmann's ring closure (p. 353). Illustrated with *m*-bromophenylparaconic acid, which gives a yield of 10 percent of 1,6-bromonaphthol, the equation is:



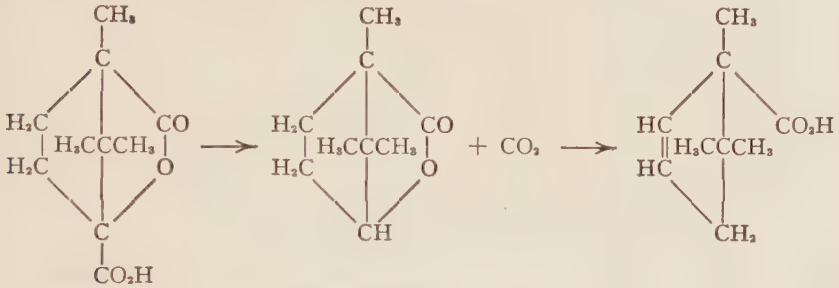
Although the yields of α-naphthols are small, the reaction has proven to be of great value in a study of the orientation of naphthalene derivatives. The centroid structure for naphthalene, according to Huggins, demands that the *peri*-positions be 1,5 instead of 1,8. Fuson proved definitely, however, by conversion of *o*-bromophenyl paraconic acid into 1,5-bromonaphthol, and subsequent conversion of this compound by the Grignard reaction to 1,5-hydroxynaphthoic acid, that the latter was identical in all respects to the so-called "1,5-hydroxynaphthoic acid", whose structure had been questioned.

Carboxyl Attached to the γ-Carbon. Apparently this type of compound has not been investigated as thoroughly as the others. At 180°, phthalid-carboxylic acid [166] is rapidly decarboxylated:



[164] Erdmann and Kirchhoff, *Ann.* **247**, 366 (1888).
[165] Fuson, *J. Am. Chem. Soc.* **46**, 2783 (1924); **47**, 516 (1925).
[166] Scherks, *Ber.* **18**, 383 (1885).

Camphanic acid [167] is decarboxylated to campholactone, part of which then rearranges into lauronolic acid.

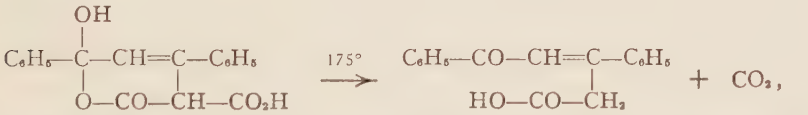


Camphanic Acid *Campholactone* *Lauronolic Acid*

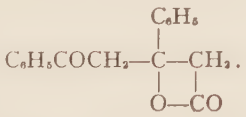
A hydrocarbon, C_8H_{14}, is also a product of this reaction; the hydrocarbon, laurolene, is related to 1,1-dimethyl-cyclohexane since it forms the latter on reduction.

δ-Lactonic Acids.

α-Carboxyl. It might be anticipated that these compounds would resemble the analogous α-carboxylated-γ-lactonic acids, and it is true that the chief reaction is one of decarboxylation. In the following reaction:



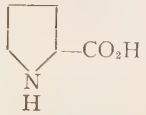
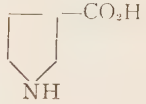
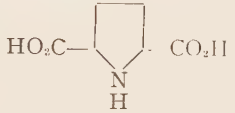
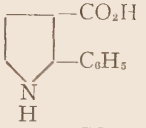
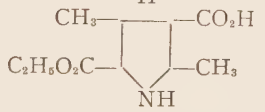
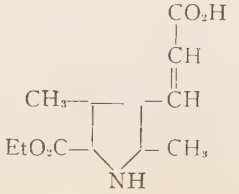
Kohler [168] observed a 40 percent yield of γ-benzoyl-β-phenylvinyl-acetic acid, and less than 0.5 percent of an isomeric β-lactone:

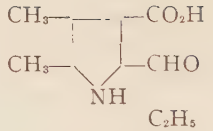
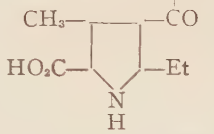
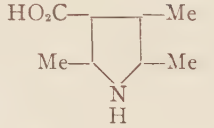
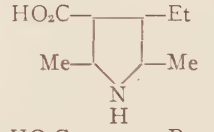
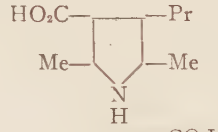
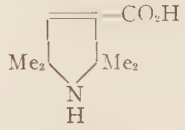


γ-Carboxyl. The behavior [169] of δ-caprolactone-γ-carboxylic acid, when distilled, is reminiscent of the conversion of the paraconic acids into unsaturated acids; γ-ethylidene butyric acid is made in this manner:

[167] Fittig and Woringer, *Ann.* **227**, 6 (1885). Aschan, *Ber.* **27**, 3504 (1894).
[168] Kohler, *Am. Chem. J.* **46**, 476 (1911).
[169] Fichter, *Ber.* **29**, 2369 (1896).

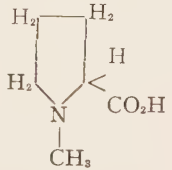
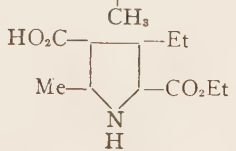
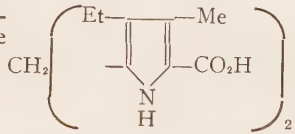
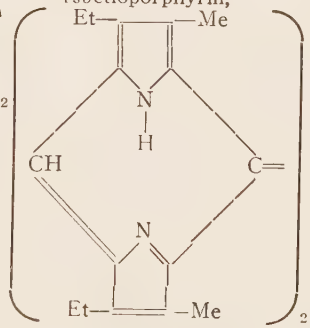
TABLE XXXIX. *Decarboxylation of Acids Related to Pyrrole and Pyridine.*

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Pyrrole-α-c a *		Pyrrole	190° (melting point) sealed tube	Schwanert, *Ann.* **116**, 275 (1860).
Pyrrole-β-c a		Pyrrole (partially)	161° (melting point) sealed tube	Ciamician, *Monatsh.* **1**, 625 (1880); *Ber.* **14**, 2055 (1881).
Pyrrole-α,α-di-c a		Pyrrole, and charring	260°, melting point	Ciamician and Silber, *Ber.* **19**, 1959 (1886).
2-Phenylpyrrole-3-c a		2-Phenylpyrrole	192°	Kondo and Suzuki, *J. Pharm. Soc. Japan*, No. **544**, 501 (1927); *Chem. Abstracts* **21**, 3362.
2,4-Dimethyl-5-carbethoxypyrrole-3-c a		Ethyl 3,5-dimethyl-pyrrole-2-carboxylate	Heat at atmospheric pressure 70 percent yield	Fischer and Walach, *Ber.* **58**, 2818 (1925).
2,4-Dimethyl-5-carbethoxypyrrole-3-β-acrylic acid		Ethyl 3,5-dimethyl-4-vinylpyrrole-2-carboxylate	Heat in 1 gram portions at 12-15 mm. and 220°; 70 percent yield	*Ibid.*

2,3-Dimethyl-5-formyl-pyrrole-4-c a		2,3-Dimethyl-pyrrole	280° and 140 mm.; sublimes out in 5 percent yield	Fischer and Belber, *Ann.* **444**, 238 (1925).
2-Ethyl-4-methyl-3-propionyl-pyrrole-5-c a		2-Ethyl-4-methyl-3-propionylpyrrole	180°, melting point	Fischer and Klarer, *Ann.* **447**, 48 (1926).
2,3,5-Trimethyl-pyrrole-4-c a		2,3,5-Trimethyl-pyrrole	Distillation; decomposes at 198°; quantitative yield	Knorr and Hess, *Ber.* **44**, 2758 (1911).
2,5-Dimethyl-3-ethyl-pyrrole-4-c a		2,5-Dimethyl-3-ethyl-pyrrole	Decomposes at 200°	*Ibid.*
2,5-Dimethyl-3-propyl-pyrrole-4-c a		2,5-Dimethyl-3-propyl-pyrrole	Decomposes at 210°; then distillation	*Ibid.*
2,2,5,5-Tetramethyl-pyrroline-3-c a		Tetramethyl-pyrroline, and charring	At melting point, 300°	Pauly and Hultenschmidt, *Ber.* **36**, 3371 (1903).

* The abbreviation "-c a" represents "-carboxylic acid."

TABLE XXXIX. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
N-methylpyrrolidine-α-c a. "Hygrinic acid"		*N*-methylpyrrolidine; 70 percent yield	Melting point, 164-9°	Liebermann and Cybulski, *Ber.* **28**, 582 (1895).
Ethyl 2-methyl-4-ethylpyrrole-3-carboxy-5-carboxylate		Ethyl 2-methyl-4-ethylpyrrole-5-carboxylate	At 245°, melting point	H. Fischer and Stangler, *Ann.* **459**, 53 (1927).
Bis-(3-ethyl-4-methyl-5-c a-pyrryl)-methane		*Iso*etioporphyrin, 	20 hours at 100°; yield, 0.035 gram from 0.8 gram	H. Fischer and Halbig, *Ann.* **448**, 193 (1926).

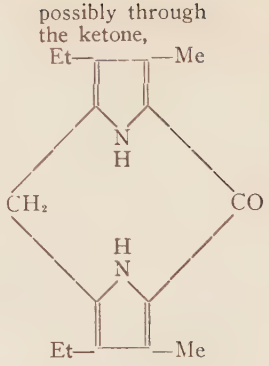
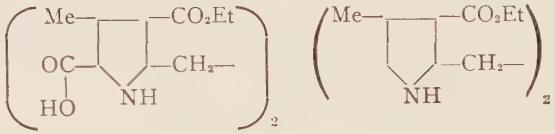
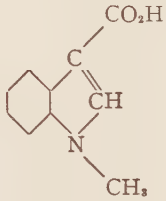
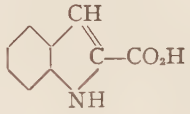
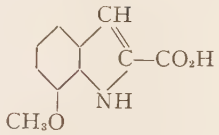
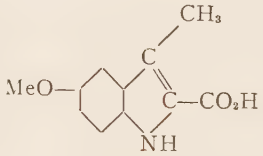
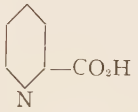
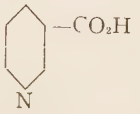
	possibly through the ketone, 			
Bis-(3-carbethoxy-4-methyl-5-carboxyl-2-pyrryl) ethane			180-200° in vacuum; 43 percent yield	Fischer and Halbig, *Ann.* **447**, 123 (1926).
Methylindole-c a		*N*-methyl indole	205°; 76 percent yield	Fischer and Hess, *Ber.* **17**, 562 (1884).
Indole-α-c a		Indole	Above melting point, 203°, or, at 230°	Reissert, *Ber.* **30**, 1045 (1897). Fischer, *Ann.* **236**, 144 (1886).

TABLE XXXIX. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
7-Methoxyindole-2-c a		7-Methoxyindole	230-233°; 70 percent yield	Blaikie and Perkin, Jr., *J. Chem. Soc.* **125**, 296 (1924).
5-Methoxyindole-2-c a	(similar)	5-Methoxyindole	205-210°	*Ibid.*
4-Methoxyindole-2-c a	(similar)	4-Methoxyindole	245-250°	*Ibid.*
5-Methoxyskatole-2-c a		5-Methoxyskatole	210°; 77 percent yield	*Ibid.*
7-Methoxyskatole-2-c a	(similar)	7-Methoxyskatole	210°	*Ibid.*
Picolinic acid		.....	Sublimes without much pyrolysis by ordinary heating.	
Nicotinic acid		.....	*Ibid.*	

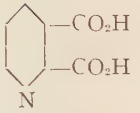
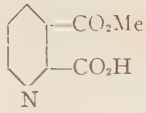
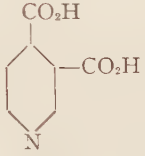
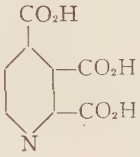
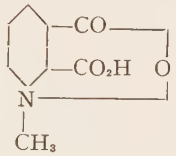
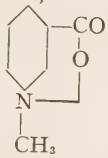
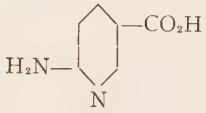
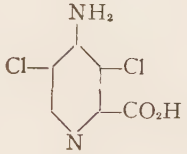
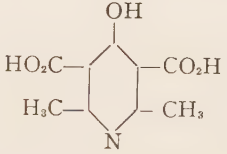
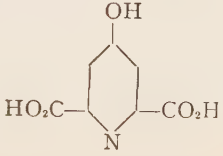
*Iso*nicotinic acid		Pyridine, partially; the rest sublimes	Heat in open dish	Ladenburg, *Ber.* **32**, 46 (1899).
Quinolinic acid		Nicotinic acid	190-210°	Skraup, *Monatsh.* **2**, 157 (1881).
		In good yields		Camps, *Arch. Pharm.* **240**, 353 (1902).
(Note the preferential elimination of the α-carboxyl.)		(The ethyl benzoate method has been checked by Hurd and Webb)	Heat in ethyl benzoate solution	U. of Ill. Bull. (1922), Organic Chemical Reagents, **IV**, 39.
β-Methyl quinolate		Methyl nicotinate	130°	Kirpal, *Monatsh.* **20**, 766 (1899).
Cinchomeronic acid		Mixture of nicotinic and *iso*nicotinic acids	At 170°, or by heating in quinoline	Camps, *loc. cit.*
α-Carbocinchomeronic acid		Cinchomeronic acid (the α-carboxyl eliminated)	By heating alone, or by 2-3 days' heating with acetic acid + 10 percent acetic anhydride	Hoogewerff and van Dorp, *Ann.* **204**, 106 (1880).
				Weidel and Brix, *Monatsh.* **3**, 604 (1882).

TABLE XXXIX. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Quinolinic acid methyl-β-betaine		Trigonellin, 	Boiling in alcohol	Kirpal, *Monatsh.* **22**, 361 (1901).
6-Aminonicotinic acid		α-Amino-pyridine	Heat	Marckwald, *Ber.* **27**, 1320 (1894).
3,5-Dichloro-4-aminopicolinic acid		3,5-Dichloro-4-amino-pyridine	A few degrees above melting point, 172°	Sell, *J. Chem. Soc.* **99**, 1679 (1911).
2,6-Dimethyl-4-hydroxy-dinicotinic acid		Dimethyl-hydroxy-pyridine	270-290°; or pyrolysis of the silver salt	Conrad and Guthzeit, *Ber.* **20**, 156 (1887).
Chelidamic acid		γ-Pyridone	At melting point, 248°	Haitinger and Leiben, *Monatsh.* **6**, 300 (1885). Lerch, *ibid.*, **5**, 402 (1884).

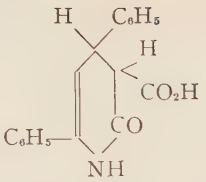
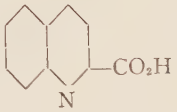
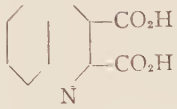
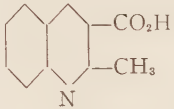
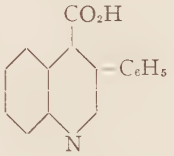
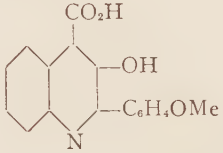
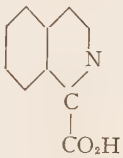
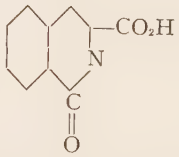
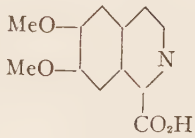
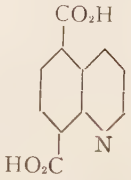
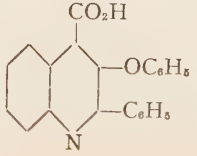
2-Keto-4,6-diphenyl-tetrahydropyridine-c a-3		2-Keto-4,6-diphenyl-tetrahydro-pyridine	130-150°	Kohler, Graustein and Merrill, *J. Am. Chem. Soc.* **44**, 2544 (1922).
Quinaldinic acid		Quinoline	At melting point, 156°, quantitatively	Doebner and von Miller, *Ber.* **16**, 2472 (1883).
Acridinic acid		Quinoline-β-c a	120-130°	Graebe and Caro, *Ber.* **13**, 100 (1880).
Quinaldine-β-c a		2-Methyl quinoline	At melting point, 234°	Rohde, *Ber.* **22**, 267 (1889).
β-Phenyl-cinchoninic acid		β-Phenyl quinoline	About 15° above the melting point	Hübner, *Ber.* **41**, 482 (1908).
α-p-Anisyl-β-hydroxy-cinchoninic acid		α-Anisyl-β-hydroxy quinoline	Above 190°, the melting point	Berlingozzi and Capuano, *Atti. accad. Lincei*, V, **33**, ii, 91 (1924).

TABLE XXXIX. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
*Iso*quinoline-c a-1		"Odor of" *iso*quinoline	At melting point, 162°	Reissert, *Ber.* **38**, 3429 (1905).
*Iso*carbostyril-c a-3		*Iso*carbostyril	At melting point, 320°, and some decomposition even below melting point. Also by heating the silver salt	Bamberger and Kitschelt, *Ber.* **25**, 1145 (1892).
6,7-Dimethoxy-*iso*quinoline-c a-1		6,7-Dimethoxy-*iso*quinoline	Stormily at 210°	Goldschmiedt, *Monatsh.* **8**, 522 (1887).
5,8-Quinoline-di-c a		5-Quinoline-c a and 8-Quinoline-c a	270-280°	Skraup and Brunner, *Monatsh.* **7**, 153 (1886).
2-Phenyl-3-phenoxy-quinoline-4-c a. (β-Phenoxyatophan)		2-Phenyl-3-phenoxyquinoline	232-238°	Berlingozzi and Turco, *Rend. accad. sci. Napoli* **31**, 191 (1925).

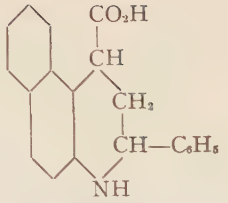
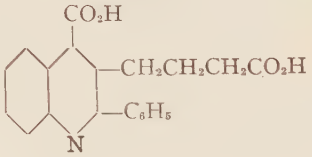
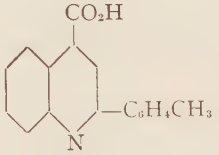
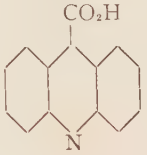
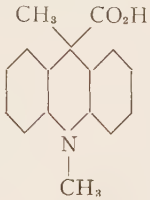
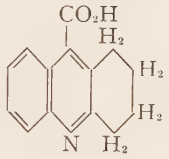
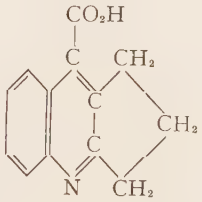
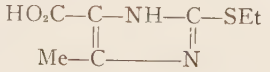
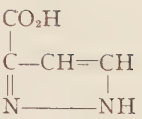
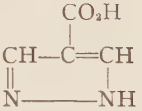
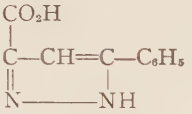
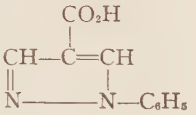
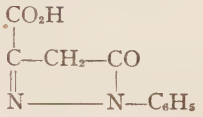
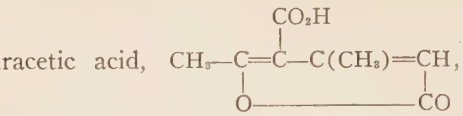
py-Tetrahydride of α-phenyl-(β)-naphthocinchoninic acid		*py*-Tetrahydride of α-phenyl-(β)-naphthoquinoline	Slightly above melting point	Ciusa and Barattini, *Gazz. chim. ital.* **56**, 131 (1926).
2-Phenyl-3-(γ-carboxypropyl)-cinchoninic acid		2-Phenyl-3-(γ-carboxypropyl)-quinoline, in 60 percent yield	Heat small amounts *in vacuo*	von Braun and Brauns, *Ber.* **60**, 1257 (1927).
3,4′ (or 2,3)-diquinolyl-2-c a	.....	3,4′ (or 2,3)-Diquinolyl	205° (or 175°)	Mills and Ordish, *J. Chem. Soc.* **1928**, 81.
2-*p*-Tolyl-cinchoninic acid		2-*p*-Tolyl-quinoline, very smoothly	250-260°, *in vacuo*	von Braun and Brauns, *Ber.* **60**, 1255 (1927).
Acridine-10-c a		Acridine	Above 300°	Bernthsen and Muhlert, *Ber.* **20**, 1550 (1887).

TABLE XXXIX. (*Continued*)

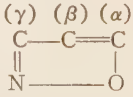
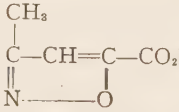
Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
5,10-Dimethyl-acridane-c a-10		5,10-Dimethyl acridane	130-160°	Kaufmann and Albertini, *Ber.* **44**, 2058 (1911).
1,2,3,4-Tetrahydro-acridine-10-c a		1,2,3,4-Tetra-hydroacridine; best method of preparation	At melting point, 284-286°	Borsche, *Ber.* **41**, 2207 (1908); *Ann.* **377**, 109 (1910).
α,β-Trimethylene-cinchoninic acid		α,β-Trimethylene quinoline	Dry distillation	Borsche, *Ann.* **377**, 121 (1910).
2-Ethylthiol-4-methyl-glyoxaline-5-c a		2-Ethylthiol-4-methylgly-oxaline	At melting point, 180°	Balaban and King, *J. Chem. Soc.* **1927**, 1867.

Pyrazole-3 (or 5) c a		Pyrazole	210-212°, melting point	Knorr, *Ann.* **279**, 231 (1894).
Pyrazole-4-c a		"Strong gas evolution, and no charring"	At melting point, 275°	Buchner and Fritsch, *Ann.* **273**, 253 (1893).
5-Phenylpyrazole-c a-3		5-(3)-Phenylpyrazole	140-150°	Buchner and Lehmann, *Ber.* **35**, 36 (1902).
1-Phenylpyrazole-c a-4		*N*-phenylpyrazole	This acid distils undecomposed, but the decarboxylation comes by 7-8 hours refluxing	Claisen, *Ann.* **295**, 320 (1897).
1-Phenylpyrazolone-5-c a-3		1-Phenylpyrazolone-5	Vacuum distillation	Stolz, *Ber.* **28**, 41 (1895).

*Iso*dehydracetic acid,  , begins to lose [170] carbon dioxide at 200° and continues to do so until 245° is reached, when "mesitene lactone", or 4,6-dimethyl-α-pyrone, distils with excellent yields. *Iso*pyromucic acid may be prepared [171] by the distillation of hydroxy-α-pyrone carboxylic acid:

N-Heterocyclic Acids.

The decarboxylation of acids which are related to pyrrole or to pyridine is such a general reaction that these will be mentioned chiefly in tabular form in Table XXXIX. The α-carboxyl is the easiest to be eliminated. (The abbreviation *-c a* will be used to represent *-carboxylic acid.*)

It is noteworthy that *is*oxazoles, with a nucleus of  , cannot be isolated by heating the corresponding acids. The decomposition is too profound, and there is much charring. This, for example, is the case [172] with α,γ-dimethyl*is*oxazole-β-carboxylic acid, or with α-methyl-*is*oxazole-γ-carboxylic acid. However, γ-methyl*is*oxazole-α-carboxylic acid,  (melting point, 211°), gives the pyridine-like odor of methyl*is*oxazole on heating, but even in this case the compound apparently is not isolable in any quantity. Small amounts of phenylmethyl-*is*oxazole, however, are obtainable by distilling small amounts of α-methyl-γ-phenyl*is*oxazole-β-carboxylic acid, a substance which is readily obtainable from ethyl benzoylacetoacetate and hydroxylamine.

Thiazoles, triazoles, pyridazines, etc., however, may be readily prepared, and these are indicated forthwith in Table XL.

[170] Hantzsch, *Ann.* **222**, 16 (1883).
[171] Blaise and Gault, *Compt. rend.* **148**, 176 (1909); *Bull. soc. chim.* **9**, 590 (1911).
[172] Claisen, *Ann.* **277**, 174 (1893); *Ber.* **42**, 60 (1909).

TABLE XL. *Preparation of Thiazoles, Triazoles, Pyridazines and Similar Compounds.*

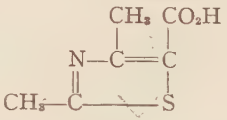
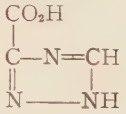
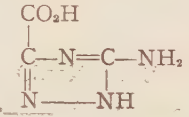
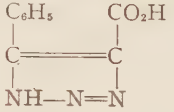
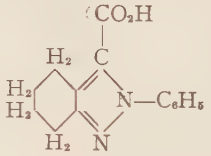
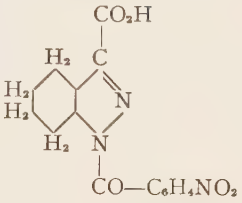
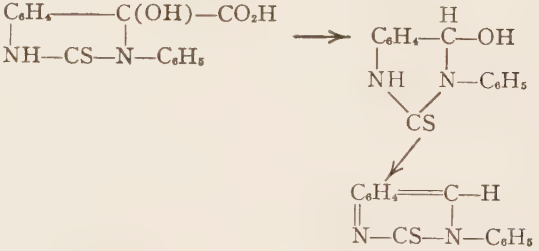
Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
2,4-Dimethyl-thiazole-5-c a		Probably, dimethyl-thiazole	CO_2 is evolved quantitatively in 10 minutes at 250°; the melting point is 124°	Smith, Flack and Inggs, *S. Afr. J. Sci.* **21**, 227 (1924); *Chem. Abstracts* **19**, 1706.
1,2,4-Triazole-3 (or 5)-c a		1,2,4-Triazole	Boiling water	Andreocci, *Ber.* **25**, 229 (1892).
5 (or 3)-Amino-1,2,4-triazole-c a-3 (or 5)		3 (or 5)-Amino-triazole	Near melting point, 182-185°	Thiele and Manchot, *Ann.* **303**, 54 (1898). Curtius, Darapsky and Müller, *Ber.* **40**, 819 (1907).
C-Phenylosotriazole-c a		C-Phenyltriazole	210-215° 205-206°	Oliveri-Mandala and Coppola, *Gazz. chim. ital.* **40**, II, 440 (1910). Oliveri-Mandala and Coppola, *Atti. accad. Lincei*, **19**, I, 563 (1910).
2-Phenyl-4,5,6,7-tetrahydroindazole-3-c a		2-Phenyl-tetra-hydroindazole	Dry distillation	von Auwers, *Ann.* **453**, 226 (1927).

TABLE XL. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
1-(*o*-Nitrobenzoyl)-4,5,6,7-tetrahydroindazole-3-c a		1-(*o*-Nitrobenzoyl)-tetrahydroindazole	Quick vacuum distillation	*Ibid.*, p. 232.
2-Thio-3-phenyl-4-hydroxy-1,2,3,4-tetrahydroquinazoline-4-c a			*	Reissert and Schaaf, *Ber.* **59**, 2494 (1926).
Pyridazine-3-c a		Pyridazine, smoothly	Distillation	Gabriel and Colman, *Ber.* **32**, 418 (1899).

* The 2-thio-3-phenyl-4-hydroxytetrahydroquinazoline is prepared by boiling the acid in an indifferent solvent of sufficiently high boiling point, followed by boiling in glacial acetic acid (to change it from a dimolecular form into the monomolecular).

** The dihydroquinazoline derivative is formed by fusion; a molecule of water is lost.

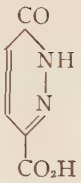
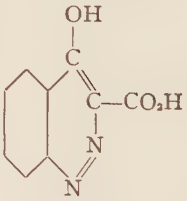
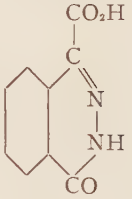
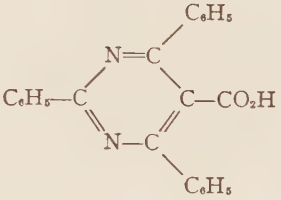
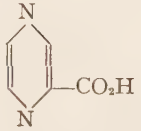
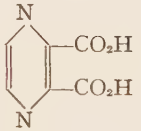
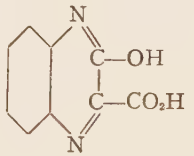
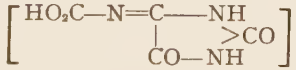
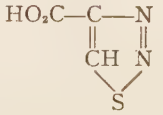
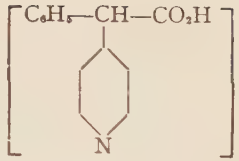
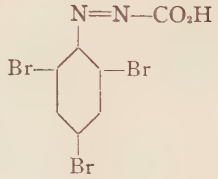
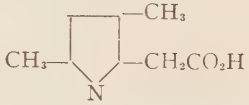
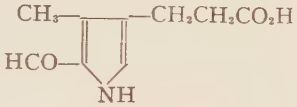
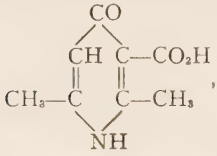
Pyridazone-c a-3		Pyridazone, quantitatively	At melting point, 260°	Gabriel, *Ber.* **42**, 657 (1909).
Hydroxy-cinnoline-c a		Hydroxycinnoline	260°	von Richter, *Ber.* **16**, 681 (1883).
Phthalazone-c a		Phthalazone	Heat	von Rothenburg, *J. prakt. Chem.* [2] **51**, 149 (1895).
2,4,6-Triphenyl-pyrimidine-c a-5		2,4,6-Triphenyl-pyrimidine yield, 1.3 grams from 2 grams	Dry distillation	Asahina and Kuroda, *Ber.* **47**, 1819 (1914).

TABLE XL. (*Continued*)

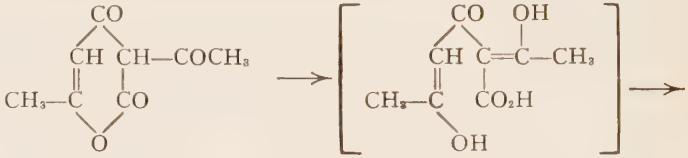
Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Pyrazine-mono-c a		Pyrazine	At melting point, 225°	Wolff, *Ber.* **26**, 723 (1893).
Pyrazine-2,3-di-c a		Pyrazine-mono-c a, and a little pyrazine	Vacuum distillation (There is "much foaming" at the melting point, 193°)	Wolff, *loc. cit.* Gabriel and Sonn, *Ber.* **40**, 4851 (1907).
3-Hydroxy-quinoxaline-2-c a		2-Hydroxy-quinoxaline	At melting point, 265°	Hinsberg, *Ann.* **292**, 248 (1896).
Allantoxaidin-*N*-c a		Allantoxaidin	Decomposes spontaneously (known only in form of salts)	Ponomarew, *Ber.* **11**, 2156 (1878). Biltz and Geisler, *Ber.* **46**, 3414 (1913).
Thio-[a b]-diazole-c a-4		Thiodiazole yield, 7 grams from 23 grams	230-260° (melting point is 228°). Use 8-gram portions	Wolff, *Ann.* **333**, 11, 18 (1904).

α-(4-Pyridyl)-phenyl-acetic acid		4-Benzyl pyridine	Decomposes spontaneously on acidifying sodium salt	Singh, *J. Chem. Soc.* **127**, 2445 (1925).
sym-Tribromobenzene-diazo-carboxylic acid		Tribromobenzene, nitrogen and carbon dioxide	Nearly spontaneously on acidifying potassium salt	Widman, *Ber.* **28**, 1931 (1895). *also* Angeli, *Chem. Abstracts* **12**, 364 (1918).
2,4-Dimethylpyrrole-5-acetic acid		Trimethylpyrrole	Distillation	H. Fischer and Rose, *Z. physiol. Chem.* **91**, 184 (1914).
2,4-Dimethylpyrrole-5-propionic acid	(similar)	Trimethylpyrrole, and a substance of the melting point, 60°	Distillation	*Ibid.*
An aldehydo-opsopyrrole-c a	 (presumably)	A porphyrin in abundance; probably coproporphyrin	At melting point, 152°	Fischer and Treibs, *Ber.* **60**, 378 (1927).

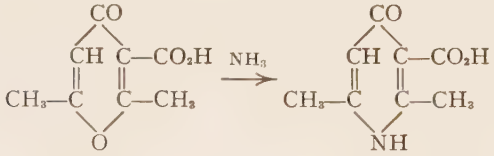
The regularity of these decarboxylations is such that they have been employed very frequently in synthetical reactions, and also they have been instrumental in the proof of structure. An especially interesting case of the latter type is the proof [173] of the structure of dehydroacetic acid. The argument is based on the fact that 3-carboxy-γ-lutidone,



, which is synthesized by accredited methods, is identical with the material which may be formed by the interaction of ammonia with an isomer (shown below) of dehydroacetic acid by the action of 85 percent sulfuric acid.

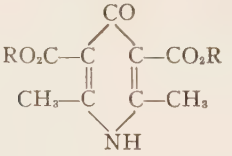


Dehydroacetic Acid

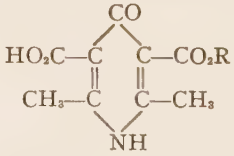


isomer of Dehydroacetic Acid — *3-Carboxy-lutidone*

Synthesis of 3,5-dicarbethoxy-γ-lutidone, and partial hydrolysis to



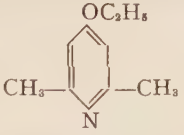
3,5-Dicarbethoxy-γ-lutidone



3-Carboxy-5-carbethoxy-γ-lutidone

3-carboxy-5-carbethoxy-γ-lutidone, make possible the formation of the ethyl ester of 3-carboxy-γ-lutidone by the pyrolysis of the 3-carboxy-5-carbethoxy-γ-lutidone. Previous efforts to duplicate these reactions in the dimethyl pyrone series were unsuccessful because it was never possible to limit the hydrolysis of the corresponding di-ester to one of the ester groups. The yield of 3-carbethoxy-γ-lutidone in the vacuum distilla-

[173] Rassweiler and Adams, *J. Am. Chem. Soc.* **46**, 2758 (1924).

tion (240° and 30 mm.) averages about 30 percent, although sometimes it is less. Almost an equal amount of ethoxy-lutidone,  , is formed simultaneously, and other simultaneous products (formed in small amounts, and not initial impurities) are 3,5-dicarbethoxy-γ-lutidone and γ-lutidone. There is also some unidentified basic material.

CHAPTER 14.

DIBASIC ACIDS.

Oxalic Acid.

Anhydrous oxalic acid [1] has long been known to evolve carbon dioxide, carbon monoxide and water in its thermal decomposition. Originally, it was thought that these substances were formed in equivalent amounts, but it has been shown that the carbon monoxide and water are formed secondarily from formic acid.[2] Under suitable conditions, two-thirds of the theoretical amount of formic acid is isolable.

The isolation of formic acid is reasonable since it has been shown (p. 332) to be fairly stable at temperatures (170°) where oxalic acid pyrolyzes readily. Calcagni [3] also reported that dry oxalic acid breaks down by heating into carbon dioxide, carbon monoxide and water, and showed that the isolated products are not formed in molecular proportions. Also, it left a residue of hydrated oxalic acid. Three concurrent reactions were suggested [4] by Berthelot and Gaudechon: (1) into carbon dioxide, carbon monoxide and water, (2) into two molecules of carbon dioxide and one of hydrogen, (3) into carbon dioxide and formic acid, which also decomposes further.

The most accurate work on the pyrolysis of anhydrous oxalic acid has been performed [5] by W. A. Noyes, Jr. At 171°, the highest temperature used, the decomposition is quite rapid. Data were also recorded for intermediate temperatures to 141°. Based on the observed pressures, it was considered that the reaction proceeds mainly to give formic acid and carbon dioxide, a reaction which is quite in harmony with other acid decarboxylations:

$$HO_2C—CO_2H \longrightarrow H—CO_2H + CO_2.$$

The decomposition occurs entirely on the surface of the oxalic acid crystals; therefore, the state of subdivision markedly influences the rate

[1] Gay Lussac, *Ann. chim.* [2] **46**, 218 (1831); *Ann.* **1**, 20 (1832); Turner, *Ann.* **1**, 25 (1832); *Ann. Physik.* **24**, 166 (1831); Berthelot, *Ann. chim.* [3] **46**, 481 (1856); Lorin, *Compt. rend.* **82**, 750 (1876); *Bull. soc. chim.* [2] **25**, 518 (1876); *Ber.* **9**, 638 (1876).

[2] Lorin, *Bull. soc. chim.* [2] **5**, 11 (1866); **37**, 107 (1882); *Compt. rend.* **93**, 1145 (1881). Cf. Gay Lussac and Turner.

[3] Calcagni, *Gazz. chim. ital.* **50**, I, 245 (1920).

[4] Berthelot and Gaudechon, *Compt. rend.* **158**, 1791 (1914).

[5] Noyes, Jr. and Wobbe, *J. Am. Chem. Soc.* **48**, 1882, 2856 (1926).

of reaction. Except with very small quantities of oxalic acid, the presence of glass wool is without noticeable effect. In Noyes' experiments, the reaction was found to be nearly of "zero" order, the constants for which are:

$$\log k_0 = 22.548 - 11227/T.$$

Photochemical decomposition of the oxalic acid was considered to have a different mechanism of activation than the thermal decomposition.

The Malonic Acid Type.

The pyrolysis of malonic acid into acetic acid is one of the best known and, as a type reaction, one of the most widely used pyrolytic reactions in organic chemistry:

$$H_2C\begin{<}{CO_2H}{CO_2H}\longrightarrow CO_2 + H_2CH{-}CO_2H.$$

It will be apparent that malonic acid and the very unstable β-ketonic acids possess a grouping in common, namely, $-CO-CH_2-CO_2H$.

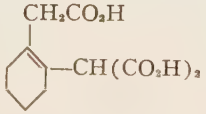
Malonic acid [6] loses carbon dioxide at 140°. Just as was observed with the β-ketonic acids, so also malonic acid is more easily decomposed in aqueous solution [7] than in the dry state; in solution, malonic acid changes into acetic at as low a temperature as 70°.

At moderately high temperatures, the decomposition [8] of malonic acid is unimolecular, and Hinshelwood has compared the rate of this unimolecular pyrolysis of molten malonic acid above its melting point with the rate of pyrolysis of supercooled liquid malonic acid below its melting point. The reaction constants in the two cases are different. Malonic acid is interesting also since it permits a comparison of reactivities of a solid system with that of a supercooled liquid system at the same temperature. Because of the decidedly different reactivity which was found, Hinshelwood states that the radiation hypothesis would lead one to anticipate a difference in the infra-red properties of the two substances.

The following table lists the data regarding some of the malonic acid analogs which have been reported in the literature. The abbreviations *c a*, for carboxylic acid, and *M*, for malonic acid, will be used. Note that the temperature for the decarboxylation is usually between 160-180°.

[6] Heintzel, *Ann.* **139**, 132 (1866).
[7] Lamouroux, *Compt. rend.* **128**, 998 (1899).
[8] Hinshelwood, *J. Chem. Soc.* **117**, 156 (1920).

TABLE XLI. *Pyrolysis of Malonic Acid Analogs.*

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Ethyl-M	$C_2H_5CH(CO_2H)_2$	Butyric acid	160°	Wislicenus and Urech, *Ann.* **165**, 95 (1873). Markownikoff, *Ann.* **182**, 332 (1876).
*Iso*propyl-M	$(CH_3)_2CH—CH(CO_2H)_2$	*Iso*valeric acid	180°	Conrad and Bischoff, *Ann.* **204**, 151 (1880).
*Iso*butyl-M	$(CH_3)_2CHCH_2CH(CO_2H)_2$	*Iso*caproic acid	Above melting point, 107°	Guthzeit, *Ann.* **209**, 236 (1881).
Dicarboxy-glutaric acid	$CH_2(CH(CO_2H)_2)_2$	Glutaric acid	At melting point, 167°	Conrad and Guthzeit, *Ann.* **222**, 258 (1883).
γ-Phenylpropyl-M	$C_6H_5(CH_2)_2—CH(CO_2H)_2$	δ-Phenyl valeric acid	160-170°	Jones and Pyman, *J. Chem. Soc.* **127**, 2588 (1925).
Cyclohexyl-M (melting point, 183°)	$C_6H_{11}—CH(CO_2H)_2$	Cyclohexylacetic acid	2-3 hours at 20-30° above melting point	Hiers with Adams, *J. Am. Chem. Soc.* **48**, 2391 (1926).
Homologs of cyclohexyl-M (melting point, 88° to 130°)	$C_6H_{11}—(CH_2)_{1\text{-}6}—CH(CO_2H)_2$	Cyclohexylpropionic to cyclohexylcaprylic acids	*Ibid.*	*Ibid.*
Δ^1-Cyclohexene-1-acetic acid-2-M (melting point, 210°)		Δ^1-Cyclohexene-1,2-diacetic acid	215° for 15 min.	Baker, *J. Chem. Soc.* **127**, 985 (1925).
Tartronic acid	$HO—CH(CO_2H)_2$	Glycollic acid or its anhydrides	About 185°	Conrad and Bischoff, *Ann.* **209**, 227 (1881).
Ethoxy-M (melting point, 123°)	$C_2H_5O—CH(CO_2H)_2$	Ethoxyacetic acid	135°	Wislicenus and Münzesheimer, *Ber.* **31**, 551 (1898).

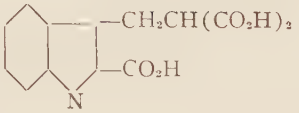
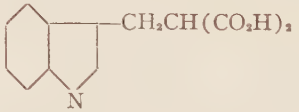
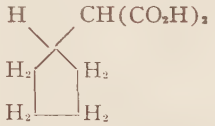
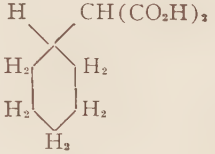
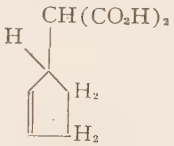
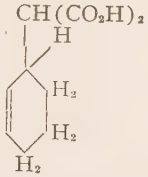
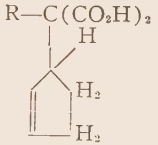
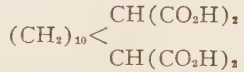
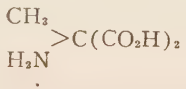
Monoethyl ester of malonic acid	$HO_2C—CH_2—CO_2C_2H_5$	Carbon dioxide, acetic acid, ethyl acetate and diethyl malonate (a disproportionation)	150°	Marguery, *Bull. soc. chim.* [3] **33**, 544 (1905).
2-Carboxy-3-(β,β-dicarboxyethyl)-indole		2-Carboxyindole-3-propionic acid (90 percent yield)	200°	Maurer and Moser, *Z. physiol. Chem.* **161**, 131 (1926).
Ibid.	*Ibid.*	Indole-3-propionic acid	215°	*Ibid.*
3-(β,β-Dicarboxyethyl)-indole		Indole-3-propionic acid	190°	*Ibid.*
10,11-Undecenyl-M	$CH_2=CH(CH_2)_8—CH(CO_2H)_2$	12,13-Tridecenoic acid	150°	Tomecko with Adams, *J. Am. Chem. Soc.* **49**, 528 (1927).
Cyclopentyl-M		Cyclopentylacetic acid	At melting point, 162-163°	Verwey, *Ber.* **29**, 1996 (1896).
Cyclohexyl-M		Cyclohexylacetic acid	180-200°	Freundler and Damond, *Compt. rend.* **141**, 594 (1905); *Bull. soc. chim.* **35**, 545 (1906). Hope and Perkin, *J. Chem. Soc.* **95**, 1363 (1909).
			Vacuum distillation	Eijkman, *Chem. Weekblad.* **6**, 699 (1908); *Chem. Zentr.* **1909**, II, 2146; *Chem. Abstracts.* **5**, 1416 (1911).

TABLE XLI. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Δ^3-Cyclopentene-M		Δ^3-Cyclopenteneacetic acid	Vacuum distillation	Eijkman, *ibid.*
Δ^3-Cyclohexene-M		Δ^3-Cyclohexeneacetic acid and some of a lactone	Vacuum distillation	*Ibid.*
Alkyl-Δ^2-cyclopentene-M		Alkyl-Δ^2-cyclopentene acetic acid (Closely related to chaulmoogric acid)	A little above melting point till CO_2 is no longer evolved	Perkins and Cruz, *J. Am. Chem. Soc.* **49**, 521 (1927).
R=ethyl *n*-propyl *iso*propyl allyl *n*-butyl cyclopentenyl			Melting point, 156° 153° 178° 146° 134° 184°	
Docedamethylene-tetra-c a		Dodecamethylene di-c a	Above melting point, 128°	Franke and Hankam, *Monatsh.* **31**, 177 (1910).
Aminomethyl-M		Alanine	Heat	Lutz, *J. Russ. Phys. Chem. Soc.* **41**, 149 (1910); *Chem. Abstracts* **5**, 1418 (1911).

Aminobenzyl-M	C_7H_7 H_2N $>C(CO_2H)_2$	Phenylalanine	Heat	*Ibid.*
Dibromo-M	$Br_2C(CO_2H)_2$	Dibromoacetic acid	At 130°, or even by warm water	Willstätter, *Ber.* **35**, 1375 (1902).
Bromoethyl-M	$C_2H_5CBr(CO_2H)_2$	α-Bromobutyric acid	At melting point, 104°	Conrad and Brückner, *Ber.* **24**, 3005 (1891).
Hydroxy-methyl-M	CH_3 HO $>C(CO_2H)_2$	Lactic acid (racemic)	160°, or, in water at 100°	Schmöger, *J. prakt. Chem.* [2] **14**, 77 (1876). Denis, *Am. Chem. J.*, **38**, 589 (1907).
Hydroxy-ethyl-M	$C_2H_5—C(CO_2H)_2$ $\vert$ OH	α-Hydroxy-butyric acid	100-180°	Guthzeit, *Ann.* **209**, 233 (1881).
Hydroxy-benzyl-M	$C_7H_7—C(CO_2H)_2$ $\vert$ OH	β-Phenyl-α-hydroxy-propionic acid	160-180°	Conrad, *Ann.* **209**, 247 (1881).
Methylethyl-M	$C_2H_5—C(CO_2H)_2$ $\vert$ CH_3	Methylethylacetic acid (The optically active acid is formed if one of the carboxyls in the acid is previously neutralized with a *d*- or *l*- base)	118°, or 100° and vacuum	Conrad and Bischoff, *Ann.* **204**, 151 (1880). Neustätter, *Ann.* **351**, 311. (1907). Tijmstra Bz, *Ber.* **38**, 2165 (1905).
Propyl-allyl-M	$C_3H_7—C(CO_2H)_2$ $\vert$ $CH_2CH=CH_2$	Propylallylacetic acid	150°	Hjelt, *Ber.* **29**, 1856 (1896).
Ethyl-allyl-M	Similar	Ethylallylacetic acid	150°	*Ibid.*
*Iso*propyl-allyl-M	Similar	*Iso*propylallylacetic acid	150°	*Ibid.*

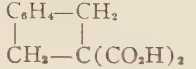
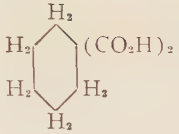
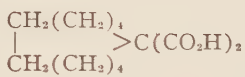
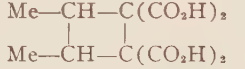
TABLE XLI. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Di-isobutyl-M	$(Me_2CHCH_2)_2C(CO_2H)_2$	Di*iso*butylacetic acid	180-200°	Freylon, *Ann. chim. phys.* **20,** 69 (1910).
n-Butyl-*iso*propyl-M	$C_4H_9C(CO_2H)_2$ $\quad\quad\vert$ $\quad CH(CH_3)_2$	*α-Iso*propyl-caproic acid	Distillation	Jones and Pyman, *J. Chem. Soc.* **120,** 2588 (1925).
Ethyl-*n*-hexyl-M	$C_6H_{13}—C(CO_2H)_2$ $\quad\quad\quad\vert$ $\quad\quad C_2H_5$	α-Ethyl-caprylic acid, quantitative yield	Distillation	Dox, *J. Am. Chem. Soc.* **47,** 3009 (1925).
Phenylethylmethyl-M	$C_6H_5CH—CH(CO_2H)_2$ $\quad\quad\quad\vert$ $\quad\quad C_2H_5$	Phenylethyl-propionic acid	150°	Reynolds, *Am. Chem. J.* **44,** 316 (1910).
Ethane-α,α,β-tri-c a	$CH(CO_2H)_2$ $\vert$ $CH_2—CO_2H$	Succinic acid	158°	Bischoff, *Ber.* **13,** 2162 (1880).
Butane-α,α,β-tri-c a	$\quad\quad CH(CO_2H)_2$ $\quad\quad\vert$ $C_2H_5—CH—CO_2H$	Ethyl-succinic acid	Distillation	Polko, *Ann.* **242,** 121 (1887).
Butane-α,β,β-tri-c a	$\quad\quad CH—CO_2H$ $\quad\quad\vert$ $C_2H_5—C(CO_2H)_2$	*Ibid.*	120-170°	Damsky, *Ber.* **19,** 3284 (1886).
Butane-β,β,γ-tri-c a	$CH_3—C(CO_2H)_2$ $\quad\quad\vert$ $CH_3—CH—CO_2H$	Dimethyl-succinic acid	160° or 200° (bath temperature)	Bischoff and Rach, *Ann.* **234,** 57 (1886). Bone and Perkin, *J. Chem. Soc.* **69,** 262 (1896).
Propane-α,α,γ-tri-c a	$CH_2CH(CO_2H)_2$ $\vert$ $CH_2—CO_2H$	Glutaric acid	At melting point, 123°	Dickens, Kon and Thorpe, *ibid.* **121,** 1501 (1922).
Pentane-α,β,β-tri-c a	$C_3H_7—C(CO_2H)_2$ $\quad\quad\vert$ $\quad CH_2—CO_2H$	Propyl-succinic acid	Heat	Lacquin, *Bull. soc. chim.* [4] **5,** 1071 (1909).

Ethane tetra-c a (melting point, 169-171°)	$\begin{matrix}CH(CO_2H)_2\\ \vert\\ CH(CO_2H)_2\end{matrix}$	Succinic acid	180°	Conrad and Guthzeit, *Ann.* **214**, 79 (1882).
Symmetrical diethyl ethane-tetracarboxylate	$\left(-CH<\begin{matrix}CO_2H\\ CO_2C_2H_5\end{matrix}\right)_2$	Ethyl succinate	180° (some at melting point, 132°)	Guthzeit, *Ann.* **214**, 74 (1882).
Propane-$\alpha,\beta,\beta,\gamma$-tetra-c a	$(HO_2C-CH_2)_2C(CO_2H)_2$	Tricarballylic acid	151°	Bischoff, *Ann.* **214**, 63 (1882).
Benzal-M	$C_6H_5CH-C(CO_2H)_2$	Cinnamic acid and some allocinnamic acid	Above melting point, 195°	Claisen and Crismer, *Ann.* **218**, 136 (1883). Liebermann, *Ber.* **26**, 1572 (1893).
Ethylene tetra-c a	$(HO_2C)_2C=C(CO_2H)_2$	Fumaric acid, or dimethylmaleic anhydride, $\begin{matrix}CH_3-C=\!=\!=C-CH_3\\ \vert\qquad\quad\diagdown\\ CO-O-CO\end{matrix}$	163°, or quick heating; especially by distillation	Bischoff, *Ber.* **29**, 1292 (1896). *Ibid.*, p. 1293.
Phenylethyl-M	$\begin{matrix}C_6H_5\\ \vert\\ CH_2CH_2CH(CO_2H)_2\end{matrix}$	Phenylbutyric acid	Distillation	Amagat, *Bull. soc. chim.* **41**, 940 (1927).
3,5-Dimethyl-4-carbethoxy-pyrrole-2-(vinyl-ω,ω-c a)	$EtO_2C-\underset{H_3C-}{\overset{}{\underset{}{\overset{-CH_3}{\underset{-CH=C(CO_2H)_2}{\overset{}{\underset{N\\H}{}}}}}}}$	CO_2, and a glassy residue; odor of dimethylpyrrole	At the melting point, 205°	Küster and others, *Ber.* **58**, 1014 (1925).
Diphenyl-hydrazino-M	$\begin{matrix}(C_6H_5)_2N-N\\ \qquad\Vert\\ (HO_2C)_2CH\end{matrix}$	CO_2, and $[(C_6H_5)_2N-N=CHCO_2H]$ (not $\downarrow$ isolated) $(C_6H_5)_2NH + [NC-CO_2H]$ (not $\downarrow$ isolated) $HCN + CO_2$	At the melting point, 164°	Staudinger and Schneider, *Helv. Chim. Acta* **6**, 316 (1923).

TABLE XLI. (*Continued*)

Name of Acid	Formula	Product Formed	Conditions of Reaction	Reference
Nitrosobenzyl-M	$C_7H_7—C(CO_2H)_2$ $\quad\quad\quad

Hydrindene-di-c a		Hydrindene-mono-c a	Distillation in free flame	Baeyer and Perkin, Jr., *Ber.* **17**, 125 (1884).
Cyclohexane-1,1-di-c a		Hexahydrobenzoic acid	Distillation	Haworth and Perkin, *J. Chem. Soc.* **65**, 103 (1894).
Hendecamethylene-di-c a		Hendecamethylene-carboxylic acid	Above melting point, 75°	Franke and Hankam, *Monatsh.* **31**, 177 (1911).
2,3-Dimethylcyclobutane-1,1,4,4-tetra-c a		2,3-Dimethylcyclobutane-1,4-di-c a (*cis* and *trans*)	180°	Vogel, *J. Chem. Soc.* **1927**, 1985.

A convenient method of synthesis[9] for diaryl-*iso*succinic acids, $Ar_2CH—CH(CO_2H)_2$, and consequently of the β,β-diaryl-propionic acids by thermal decarboxylation (180-200°), was reported recently by Baillon. It consists in heating benzohydrols for 2 hours on the water bath with malonic acid:

$$Ar_2CHOH + CH_2(CO_2H)_2 \longrightarrow Ar_2CH—CH(CO_2H)_2 + H_2O.$$

In this work, *Ar* in Ar—CHOH—Ar′ represented *p*-anisyl, 3,4-dimethoxyphenyl, 3,4-methylenedioxyphenyl, and *p*-dimethylaminophenyl; with each of these radicals, the radical *Ar′* represented phenyl, *o*- or *p*-tolyl, and α-naphthyl.

The Succinic Acid Type

(*Functional Group* $HO_2C—\overset{|}{\underset{|}{C}}—\overset{|}{\underset{|}{C}}—CO_2H$).

Quite characteristically, succinic acid is thermally dehydrated[10] into succinic anhydride, a 5-membered cyclic anhydride. At 235° the anhydride distils away, which indicates that the pyrolysis must have started at a lower temperature. In fact, at the melting point[11] (185°), in a vacuum of 50-60 mm., the same phenomenon occurs. Although pure succinic anhydride may be prepared by the repeated distillation of small quantities of the acid, larger amounts of it are usually prepared with the assistance of dehydrating agents:

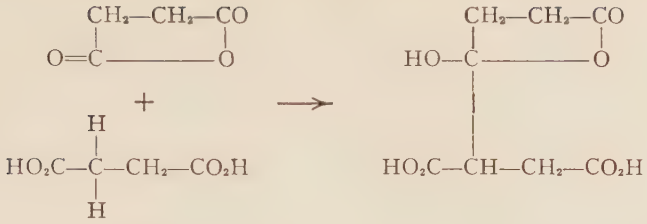
$$\begin{matrix} CH_2—CO_2H \\ | \\ CH_2—CO_2H \end{matrix} \longrightarrow \begin{matrix} CH_2—CO \\ | \quad >O \\ CH_2—CO \end{matrix} + H_2O.$$

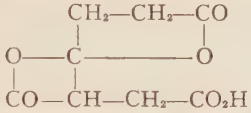
Succinic anhydride undergoes a further change if it is refluxed for 5-6 hours. Carbon dioxide is eliminated[12] and the dilactone of acetone diacetic acid (hydrochelidonic acid) is produced in 40-46 percent yields:

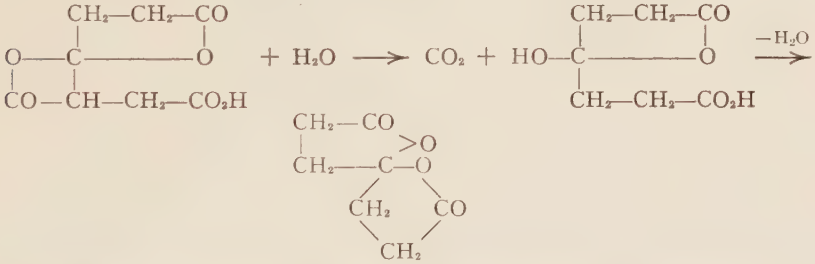
$$2\ \begin{matrix} CH_2—CO \\ | \quad >O \\ CH_2—CO \end{matrix} \longrightarrow \begin{matrix} CH_2—CO \\ | \quad >O \\ CH_2—C—O \\ \quad\quad / \quad \backslash \\ \quad CH_2 \quad CO \\ \quad\quad \backslash \quad / \\ \quad\quad CH_2 \end{matrix} + CO_2.$$

This dilactone may be separated from the admixed succinic anhydride by its far greater solubility in chloroform. Volhard's experiments were apparently performed with 70 percent anhydride, and his first suggestion of the reaction mechanism[13] necessitated the presence of succinic acid:

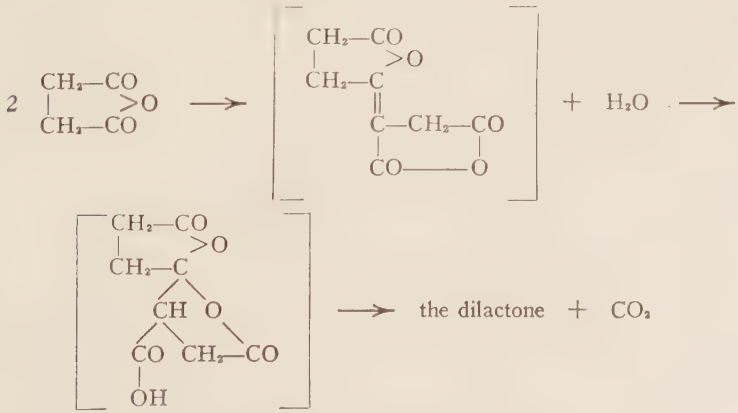
[9] Baillon, *Ann. chim.* **15**, 61-108 (1921).
[10] D'Arcet, *Ann. chim.* [2] **58**, 288 (1835).
[11] Krafft and Noerdlinger, *Ber.* **22**, 816 (1889).
[12] Volhard, *Ann.* **253**, 206-209 (1889).
[13] Volhard, *ibid.*, p. 233.



From this point the β-hydroxy acid was considered to be dehydrated to the β-lactone,  . Since all attempts to prepare β-lactones by this means have resulted in total failure, this step seems quite inadequate. Furthermore, the following steps, suggested by Volhard, seem equally fanciful.



Because of a criticism by Bredt,[14] Volhard discarded this mechanism in favor of the following, which uses only succinic anhydride as a beginning material in the formulation:

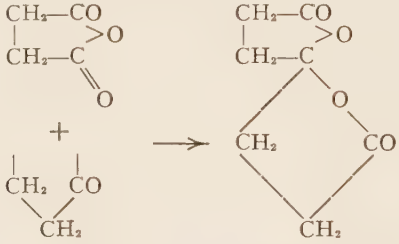


None of the intermediate steps was realized.

[14] Bredt, *Ann.* **256**, 330 (1890). Volhard, *Ann.* **267**, 60 and 94 (1891).

It has been found [15] in the author's laboratory that purified succinic anhydride (Volhard used anhydride of 70 percent purity) gives a 41-42 percent yield of purified dilactone, if the anhydride is heated for 6 hours at 250-280°. This establishes rather definitely that Volhard's first mechanism is incorrect. In the absence of evidence to the contrary, it would seem that a much more direct mechanism than Volhard's later formulation would be to assume intermediate elimination of carbon dioxide from part of the succinic anhydride molecules, and the subsequent attachment of the residue, [—CH_2—CH_2—CO—], to the carbonyl group of some of the undecomposed anhydride molecules. Thus:

and then,

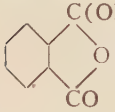


Later experiments may find this mechanism unsatisfactory, but at present it has the merit of explaining the observed facts with fewer assumptions than the others.

A possible argument against this mechanism is the fact that the residue, (—CH_2—CH_2—CO—), should be able to satisfy its free valences in more ways than one. For example, it might be expected to attach itself to both carbonyl groups in the anhydride molecule. Possibly it does so; at least, the reaction product after the 6 hours of refluxing is a brown, tarry mass. It might also be expected to polymerize to cyclohexanedione, $CO(CH_2—CH_2)_2CO$, but this substance is not to be found among the reaction products (Hurd and Bennett). However, it is pertinent to note that Feist [16] only obtained 0.4 gram of cyclohexanedione from the pyrolysis of 1 kg. of calcium succinate (*q. v.*), so that it should scarcely be anticipated in the case of succinic anhydride.

Roser's experiment [17] with a mixture of phthalic anhydride (3 parts), succinic anhydride (3 parts), and sodium acetate (1 part) is somewhat analogous. There is no reaction when this mixture is heated

[15] Hurd and Bennett, unpublished results.
[16] Feist, *Ber.* **28**, 739 (1895).
[17] Roser, *Ber.* **17**, 2770 (1884).

in an oil bath at 200°, but the reaction giving the dilactone related to β-benzoyl-propiono-*o*-carboxylic acid, $C_6H_4(CO{-}O)(O{-}CO){-}CH_2{-}CH_2$, is complete in one hour at 240-250°. Roser explained the results by first assuming an addition compound of phthalic anhydride and succinic acid,  , but here again a more direct explanation is to assume the addition of the residue, $(CH_2{-}CH_2{-}CO{-})$, to the carbonyl group of phthalic anhydride.

Cis-Hexahydrophthalic anhydride, $CH_2{-}CH_2{-}CH(CO){-}CH_2{-}CH_2{-}CH(CO)>O$ has been found[18] to undergo pyrolysis at 380° into carbon dioxide, water and anthraquinone together with various hydrogenated derivatives of anthracene. Good evidence[19] for the existence of the residue, $[CH_2{-}CH_2{-}CH(CO){-}CH_2{-}CH_2{-}CH{-}]$ is apparent in the isolation of dodecahydro-anthraquinone, $C_6H_{10}{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_{10}$. The similarity is noted between this case and Feist's isolation of cyclohexanedione.

Homologs of succinic acid also form anhydrides when they are heated. Thus, methylsuccinic acid, commonly called pyrotartaric acid because of its pyrolytic formation from tartaric acid, changes[20] into pyrotartaric anhydride at 200°:

$$CH_3{-}CH(CO_2H){-}CH_2{-}CO_2H \longrightarrow CH_3{-}CH(CO){-}CH_2{-}CO{>}O + H_2O.$$

Ethylsuccinic acid[21] and α,α-dimethyl-succinic acid[22] form their anhydrides by heating. Both α,β-dimethyl-succinic acid[23] and α-methyl-β-ethyl-succinic acid,[24] $R{-}CH(CO_2H){-}CH(CO_2H){-}R$, exist in diastereoisomeric modifications, the high melting form of each fusing 80° higher than the corresponding low melting form. The high melting acids change into

[18] Windaus, Huckel and Reverey, *Ber.* **56**, 91 (1923).
[19] Windaus and Ehrenstein, *Nachr. kgl. Ges. Wiss. Göttingen*, Math-Phys. Klasse, **1922**, 1; *Chem. Abstracts*, **17**, 1431.
[20] Markownikow, *Ann.* **182**, 328 (1876).
[21] Polko, *Ann.* **242**, 122 (1887).
[22] Pinner, *Ber.* **15**, 582 (1882).
[23] Zelinsky, *Ber.* **21**, 3170 (1888); Bone and Perkin, *J. Chem. Soc.* **69**, 262 (1896); Fittig, *Ann.* **304**, 178 (1899).
[24] von Auwers and Fritzweiler, *Ann.* **298**, 162 (1897).

their anhydrides slightly above their melting points, but further heating of these anhydrides rapidly isomerizes them to the anhydrides of the low-melting acids. Thermal dehydration of the low melting acids leads exclusively to their anhydrides. Tetraethyl succinic acid [25] changes into its anhydride by melting (149°). The high melting form [26] of α-phenyl-α′-methyl-succinic acid (melting point 192°) changes into an anhydride above its melting point. This anhydride, which may be distilled at 310-320°, or at 184° and 10 mm., gives a mixture of the high and the low melting acids when it reacts with water.

At its melting point, 73-75°, diphenylene succinic acid,[27]

$$\begin{matrix} C_6H_4 & & CH_2{-}CO_2H \\ | & >C< & \\ C_6H_4 & & CO_2H \end{matrix},$$

begins to change into its anhydride. With 1-methylcyclohexane-2-acetic-2-carboxylic acid,

$$\begin{matrix} & & & & CH_2{-}CH_2{-}CH{-}CH_3 & & \\ & & & & | & & \\ CH_2{-}CH_2{-}C{-}CH_2{-}CO_2H & & & & & & \\ | & & & & & & \\ CO_2H & & & & & & \end{matrix},$$

there is a quantitative formation [28] of its anhydride.

Either the *cis* or the *trans* form [29] of 2,3-dimethyl-cyclobutane-1,4-dicarboxylic acid,

$$\begin{matrix} CH_3{-}CH{-}CH{-}CO_2H \\ | \quad\quad | \\ CH_3{-}CH{-}CH{-}CO_2H \end{matrix},$$

by distillation *in vacuo,* gives a distillate which contains only the *cis* acid, together with some of its anhydride. This is the best way to prepare the pure *cis* acid.

This type of pyrolysis is also characteristic of aromatic compounds that incorporate the two central carbon atoms of this functional group in the aromatic nucleus, such as phthalic acid, but is never observed when the functional group forms part of a *N*-heterocyclic nucleus. It will be shown that this type of dicarboxylic acid always loses carbon dioxide by heat. So characteristic is the formation of cyclic anhydrides from dibasic anhydrides related to succinic that the reaction has been of considerable value in the determination of structure. As will be emphasized later, compounds related to glutaric acid behave analogously, but in this case, the cyclic anhydride which is produced contains a 6-membered ring.

Maleic acid, a compound which is closely related to succinic acid, melts at 130°; about 30° above this it commences to change into maleic anhydride.[30] This reaction is, of course, reversible at lower tempera-

[25] Walker and Walker, *J. Chem. Soc.,* **87**, 964 (1905).
[26] Zelinsky and Buchstab, *Ber.* **24**, 1878 (1891); Ruhemann, *J. Chem. Soc.* **81**, 1216 (1902).
[27] Wislicenus and Mocker, *Ber.* **46**, 2772 (1913).
[28] Hückel and Wiebke, *Ber.* **59**, 2844 (1926).
[29] Vogel, *J. Chem. Soc.* **1927**, 1985.
[30] Reicher, *Rec. trav. chim.* **2**, 312 (1883).

tures. Fumaric acid undergoes a transformation [31] into maleic anhydride between 230-300° with some charring. Quite analogously, diphenyl maleic anhydride [32] is produced when diphenyl fumaric acid is heated to 240°. Diphenyl maleic acid does not exist.

It has already been mentioned on p. 351 that aconitic acid, $HO_2C{-}CH{=}C(CO_2H){-}CH_2{-}CO_2H$, changes readily into aconitic anhydride, $HO_2C{-}CH{=}C(CO){-}CH_2{-}CO{>}O$, by the methods of pyrolysis. Phenyl itaconic acid, $C_6H_5CH{=}C(CO_2H){-}CH_2{-}CO_2H$, is converted into its anhydride [33] by fusion (164°), and repeated fusions produce a small amount (3-4 percent) of the lower melting isomer, phenyl citraconic anhydride, $C_6H_5{-}CH_2{-}C(CO){=}CH{-}CO{>}O$. Since this compound is instantly rearranged into phenylitaconic anhydride at 165°, this is evidence of an equilibrium which is largely on the phenylitaconic side. This is interesting in view of the fact [34] that citraconic anhydride is formed by distilling itaconic anhydride at ordinary pressure:

$$CH_2{=}C(CO){-}CH_2{-}CO{>}O \longrightarrow CH_3{-}C(CO){=}CH{-}CO{>}O.$$

Apparently, these two cases are dissimilar, yet there is the very essential point of similarity that the conjugate linkages still remain, and that the position of the new double bond is midway between the two terminal double bonds of the conjugate system in each case. Citraconic anhydride may be isolated in 30 percent yield by distilling [35] anhydrous citric acid.

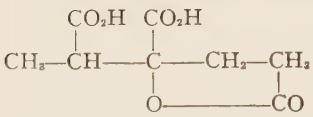
Some dibasic acids, which contain the functional group for succinic acid, fail to form their anhydrides because of the overpowering influence of other functional groups in the molecule. Diacetyl succinic acid,[36] for example, is not only related to succinic acid, but it is also a β-ketonic acid. It does not occasion surprise, therefore, to learn that it decomposes by heat into acetonylacetone and carbon dioxide:

$$CH_3CO{-}CH(CO_2H){-}CH(CO_2H){-}CO{-}CH_3 \longrightarrow CH_3CO{-}CH_2{-}CH_2{-}CO{-}CH_3 + 2CO_2.$$

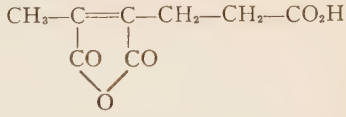
[31] Wislicenus, *Ann.* **246**, 93 (1888).
[32] Rügheimer, *Ber.* **15**, 1627 (1882).
[33] Fittig and Brooke, *Ann.* **305**, 21 (1899); Fittig, *Ber.* **26**, 45 (1893).
[34] Fittig, *Ann.* **304**, 122 (1899).
[35] Goebel, *J. Am. Chem. Soc.* **47**, 1994 (1925).
[36] Knorr, *Ber.* **33**, 1219 (1900).

Again, itadibromopyrotartaric acid is related to γ-halogen acids as well as to succinic acid. The effect of the former predominates, since [37] at 180° it lactonizes into bromohydroaconic acid (β-bromoparaconic acid, see p. 367 for such compounds):

The lactonic acid, derived from hematinic acid and hot, concentrated

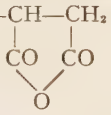
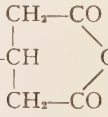


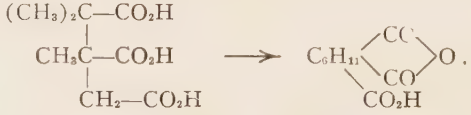
Lactonic Acid



Hematinic Acid

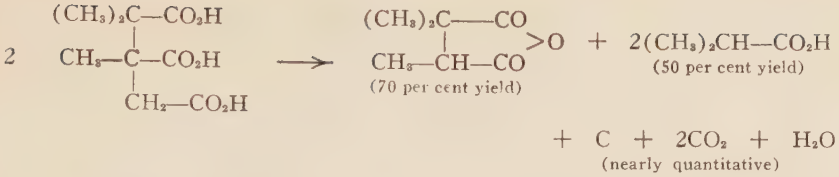
potassium hydroxide, loses carbon dioxide at 245° and changes [38] into methylethylmaleic anhydride. To account for this transformation, it is reasonable to assume that the lactonic acid reverts to hematinic acid, which then loses its carboxyl group.

Tricarballylic acid [39] behaves normally when heated, and yields the anhydro acid by distillation at low pressures. The structure of the anhydride is either  (related to succinic anhydride), or  (related to glutaric anhydride). A quantitative conversion [40] of camphoronic acid to anhydrocamphoronic acid may be effected at 180° under reduced pressure:



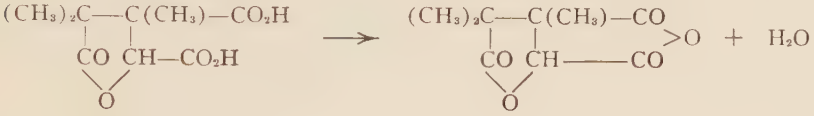
At ordinary pressure, the pyrolysis is more complex. Isolation of *iso*-butyric acid, trimethyl succinic anhydride and carbon dioxide by gradual distillation [41] of camphoronic acid guided Bredt to the elucidation of its structure. It was considered that the pyrolysis proceeded as follows:

[37] Carriere, *Ann. chim.* **17**, 93 (1921); Swarts, *Bull. acad. roy. Belg.* [2] **33**, 1872, erroneously considered bromoitaconic acid, $CHBr{=}C(CO_2H){-}CH_2{-}CO_2H$, to be the product of this reaction.
[38] Küster and Weller, *Ber.* **47**, 536 (1914).
[39] Emery, *Ber.* **24**, 596 (1891).
[40] Goebel with Noyes, *J. Am. Chem. Soc.* **45**, 3067 (1923).
[41] Bredt, *Ber.* **18**, 2990 (1885); *Ann.* **292**, 71 (1896).

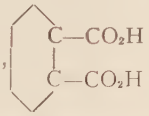


An indifferent, unidentified oil was also produced in appreciable amounts.

By vacuum distillation, *i*-camphoranic acid [42] is changed into *a*-camphoranic anhydride with elimination of water at about 160°.



Cyclobutane-1,2-dicarboxylic acid occurs in two modifications, *cis* and *trans*. The *cis*-anhydride distils at 270-273°, and this anhydride is also produced by the distillation [43] of the *trans*-acid. This behavior is also characteristic [44] of the *cis* and *trans* cyclopentane-1,2-dicarboxylic acids at 300°, and of the cyclohexane-1,2-dicarboxylic acids.[45]

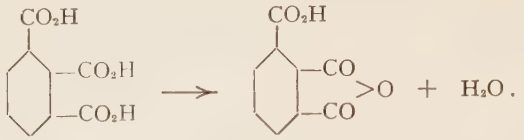
Phthalic acid, 

, possesses the functional group of succinic or of maleic acids. This acid possesses no definite melting point, since in the process of fusion, water is eliminated and phthalic anhydride is formed. Depending on the method of heating, this occurs between 180-200° but usually at about 195°. *Iso*phthalic acid and *tere*phthalic acid do not exhibit this behavior. 4-Methyl-phthalic acid,

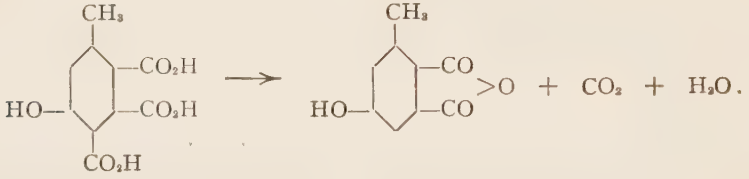
, melts [46] with decomposition at 170°, and between 170-180° its anhydride forms easily. Tetrachlorophthalic acid, $C_6Cl_4(CO_2H)_2$, also forms its anhydride [47] easily by heat. In general, the melting point of a dibasic acid of the phthalic acid type merely means the temperature at which the conversion into the anhydride has progressed sufficiently far that fusion, or perhaps better, solution, occurs.

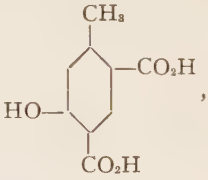
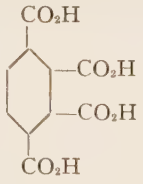
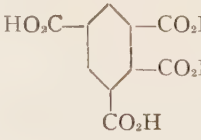
[42] Noyes and Doughty, *J. Am. Chem. Soc.* **27**, 1434 (1905).
[43] Perkin, *J. Chem. Soc.* **51**, 25 (1887); **65**, 585 (1894).
[44] Perkin, *Ber.* **18**, 3251 (1885); *J. Chem. Soc.* **51**, 244 (1887); **57**, 232 (1890); **65**, 586 (1894).
[45] Baeyer, *Ann.* **258**, 217 (1890).
[46] Helfer, *Helv. Chim. Acta* **7**, 945 (1924).
[47] Graebe, *Ann.* **238**, 322 (1887).

Hemimellitic acid is converted to an anhydride at 190°:



There is no doubt that the *ortho* groups alone [48] function in this change, since further heating to 300° causes the removal of the carboxyl and the formation of phthalic anhydride. Cochenillic acid behaves analogously at its melting point, 224°, and gives [49] the anhydride of β-coccinic acid:

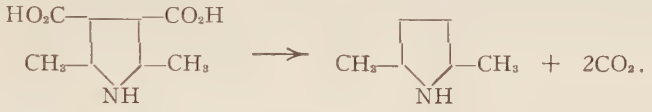


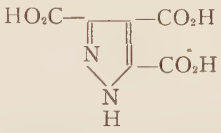
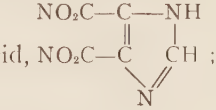
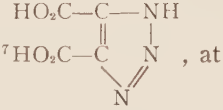
A different change occurs when cochenillic acid is heated at 170° in the presence of water; *m*-hydroxyuvitinic acid,  , results, which indicates decarboxylation of the central carboxyl. The following compounds behave in an analogous way: trimellitic acid,[50] (at 224°); prehnitic acid,  (at 239-250°); mellophanic acid,  (at 220-240°); pyromellitic acid, (at 265-286°). Mellitic acid, $C_6(CO_2H)_6$, when distilled,[51] yields pyromellitic anhydride.

[48] Graebe and Leonhardt, *Ann.* **290**, 221 (1896).
[49] Liebermann and Voswinckel, *Ber.* **30**, 688, 1731 (1897); Landau, *Ber.* **33**, 2442 (1900).
[50] Baeyer, *Ann.* **166**, 325 (1873).
[51] Baeyer, *Ann. Supplement* **7**, 35 (1870).

Even the nitrophthalic acids may be pyrolyzed to the nitrophthalic anhydrides in fairly good yields at their melting points. 3-Nitrophthalic anhydride has been prepared [52] in nearly quantitative yields by heating the acid under varying conditions (230°), but it is simpler [53] to obtain good results with the aid of acetic anhydride as a dehydrating agent. 4-Nitrophthalic acid changes [52] into its anhydride at 164-170° (melting point 164°).

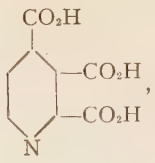
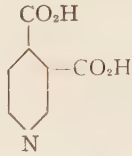
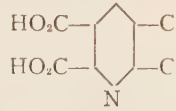
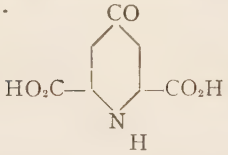
It has been shown that the elimination of water between two adjacent carboxyls in homocyclic compounds is very general. Quite the reverse is true in **heterocyclic compounds.** At the melting point, 250°, 2,5-dimethylpyrrole-3,4-dicarboxylic acid decomposes smoothly [54] into dimethylpyrrole and carbon dioxide:

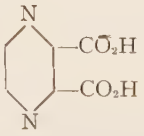


The *N*-alkyl homologs behave also in this manner. All three carboxyls are removed from pyrazole tricarboxylic acid,[55]  at 230-240°. Pyrazole is prepared in this manner. Glyoxaline [56] is similarly prepared at 300° from glyoxaline-4,5-dicarboxylic acid,  ; also, triazole from triazole dicarboxylic acid,[57]  , at 200°; and *N*-phenyl-triazole,[58] or *C*-phenyl-triazole (at 210°) from the corresponding dibasic acids. Dimroth demonstrated that by careful heating, one of the carboxyl groups can be retained in the *N*-phenyl pyrolysis.

Decarboxylation also prevails in the **pyridine series.** As was pointed out on p. 384, this process proceeds in steps since the α-carboxyl is

[52] Kahn, *Ber.* **35**, 3859 (1902).
[53] Nicolet and Bender, "Organic Syntheses," Vol. VII, New York, John Wiley and Sons, Inc., **1927**, p. 74.
[54] Knorr, *Ber.* **18**, 302, 1565 (1885); Pieroni and Veremeenco, *Gazz. chim. ital.* **56**, 455 (1926).
[55] Buchner, *Ber.* **22**, 846 (1889).
[56] Maquenne, *Ann. chim. phys.* [6] **24**, 527 (1891).
[57] Bladin, *Ber.* **26**, 546, 2737 (1893).
[58] Pechmann, *Ann.* **262**, 311 (1890); Dimroth, *Ber.* **35**, 1036 (1902); Oliveri-Mandala and Coppola, *Gazz. chim. ital.* **40**, II, 440 (1910).

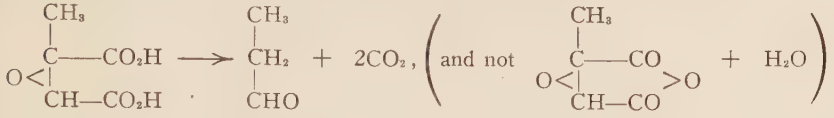
easiest eliminated. α-Carbocinchomeronic acid,  , is illustrative of this fact. Cinchomeronic acid,  , is perhaps best produced if carbocinchomeronic acid [59] is refluxed for two to three days at the boiling temperature of a mixture of glacial acetic acid and acetic anhydride (10 percent). In turn, cinchomeronic acid, which still contains the correct functional group for anhydride formation, becomes further decarboxylated at the melting point, forming a mixture of nicotinic and *iso*nicotinic acids. The tetracarboxylic acid,[60]  , loses its two α-carboxyls at 150°, and dinicotinic acid results. Chelidamic acid,  , was used by Riegel and Reinhard [61] in the synthesis of γ-pyridone by heating at atmospheric pressure (260°) till carbon dioxide evolution ceased. *N*-Methyl-γ-pyridone was prepared similarly.

Pyrazine-2,3-dicarboxylic acid,  , changes [62] into pyrazine monocarboxylic acid by vacuum distillation. A little pyrazine is formed simultaneously. At higher temperatures, especially in the presence of glacial acetic acid, pyrazine is produced in good yields.

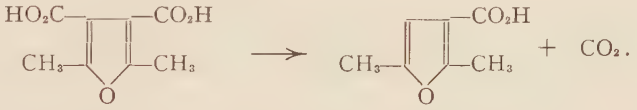
The ***O*-heterocyclic dicarboxylic acids** exhibit preferential decarboxylation, and cyclic anhydride formation is not observed. That is, there seems to be no tendency to form compounds by thermal means

[59] Weidel and Brix *Monatsh.* **3**, 604 (1882).
[60] Hantzsch and Weiss, *Ber.* **19**, 286 (1886).
[61] Riegel and Reinhard, *J. Am. Chem. Soc.* **48**, 1344 (1926); Sedgwick and Collie, *J. Chem. Soc.* **67**, 403 (1895).
[62] Gabriel and Sonn, *Ber.* **40**, 4851 (1907).

which possess bi-*O*-heterocyclic nuclei. Oxycitraconic acid decomposes [63] into propionaldehyde and carbon dioxide when heated:



Chlorocitromalic acid, $CH_3—CCl(—CO_2H)—CH(OH)—CO_2H$, undergoes the same transformation, which leads to the inference either that oxycitraconic acid, or that chloropropyl alcohol, $CH_3—CHCl—CH_2OH$, is an intermediate product. Carbopyrotritaric acid gives a sublimate [64] of pyrotritaric acid (uvic acid) when it is heated above its melting point, 230°. Thus:

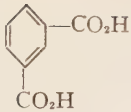


Similar derivatives in the **thiophene series** have not been thoroughly studied. In very many respects, the chemical behavior of compounds in this series behave strikingly like their benzene analogs. Whether or not thiophene-2,3-dicarboxylic acid behaves like phthalic acid, when heated, is not known. The acid [65] does not melt below 260°; at 270°, it chars and gas is evolved. A white sublimate was noticed, but nothing further regarding these products was mentioned. The 2,4-dicarboxylic acid [66] undergoes pyrolysis with some sublimation at 280°, and the 2,5-dicarboxylic acid sublimes without decomposition at 350°.

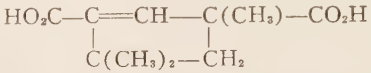
The Glutaric Acid Type.

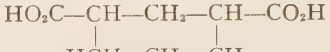
Quite generally, in open chain compounds wherein two carboxyl groups are separated by three carbon atoms, cyclic anhydride formation is induced by heat. The glutaric and the succinic acid types are similar in this respect, but important differences are apparent. Usually, the succinic dehydrations take place much more easily than the corresponding ones in the glutaric series. Furthermore, when the three central carbon atoms of the functional group, $HO_2C—C—C—C—CO_2H$, are part of a cyclic nucleus, the possibility of anhydride formation may be excluded by Bredt's rule (p. 12). Thus, neither *iso*phthalic acid,

[63] Goebel, *J. Am. Chem. Soc.* **47**, 1991 (1925).
[64] Harrow, *Ann.* **201**, 158 (1880). Fittig and von Eynern, *Ann.* **250**, 189 (1888). Referred to by Marquis, *Ann. chim.* [8] **4**, 203 (1905).
[65] Gerlach, *Ann.* **267**, 159 (1891).
[66] Gerlach, *ibid.* p. 169.

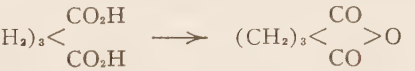


, nor dehydro*iso*fenchic acid [67] (p. 13),



both of which possess this type of unsaturation mentioned in Bredt's rule, can be induced to form an anhydride by thermal means or otherwise, although both of these acids are related to glutaric acid. The anhydride of *cis*-hexahydro*iso*phthalic acid,  , is known although it does not seem to have been prepared as yet by pyrolysis of the acid.

At 300°, glutaric acid may be distilled with very little pyrolysis if the distillation is performed rapidly. Slow distillation [11] at this temperature produces a mixture of acid and anhydride:



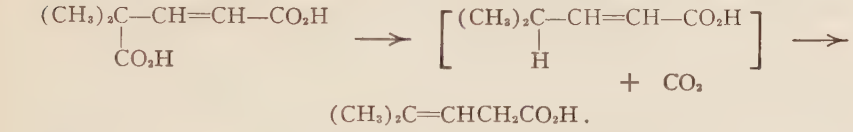
The anhydride may also be isolated after several hours' refluxing at 10 mm. pressure. Slight anhydride formation is apparent with α-methyl-glutaric acid [68] at 222°, the boiling point, at 61 mm. pressure. Komnenos [69] reported the elimination of water from β-methyl-glutaric acid by distillation (282-284°). Even with small quantities which were rapidly distilled, α-ethyl glutaric acid [68] was found to change somewhat into its anhydride at the boiling point, 250-260°.

The high melting [70] or fumaroid form of α,α′-dimethyl-glutaric acid, $CH_2(CHCH_3—CO_2H)_2$, is distillable without decomposition at 32 mm., and small amounts suffer but little change when distilled at atmospheric pressure. However, if the distillation temperature (272-275°) is approached very gradually (20 minutes for a 2-gram sample), the distillate consists almost exclusively of the anhydride. It is the anhydride of the isomeric maleinoid form [71] which is obtained, however. The longer this anhydride is refluxed up to one hour the lower is the melting point of the mass on cooling. This is an indication of decomposition, but the extent of this decomposition was shown to be almost negligible. Distillation of the low melting or maleinoid form [72] of

[67] Toivonen, *Ann.* **419**, 200 (1919).
[68] Auwers and Titherley, *Ann.* **292**, 210, 214 (1896).
[69] Komnenos, *Ann.* **218**, 152 (1883).
[70] Auwers and Thorpe, *Ann.* **285**, 325 (1895).
[71] *Ibid.*, p. 339.
[72] *Ibid.* p. 329.

α,α'-dimethylglutaric acid at 212° and 75 mm. causes a partial rearrangement into the furamoid form. At a higher pressure (205 to 245 mm.), the principal change is that of dehydration.

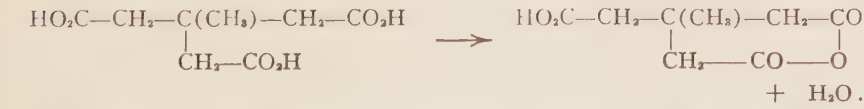
The double bond in α,α-dimethyl-glutaconic acid destroys the tendency for dehydration (see p. 353). When 3-gram samples are distilled [73] at 200° from a small retort, good yields of pyroterebic acid are obtained. Rearrangement, as well as decarboxylation, occurs. Blaise and Courtot suggested *iso*propyl acrylic acid as an intermediate product:



$$(CH_3)_2C{=}CHCH_2CO_2H\,.$$

Aromatic substituents in the glutaric acid skeleton appear to promote a more facile anhydride formation. Thus, α-phenyl-glutaric acid [74] gives a quantitative yield of its anhydride by vacuum distillation (boiling point (13 mm.) 218-230°), and the β-phenyl analog [75] behaves similarly above its melting point, 143°. In contrast, however, α-diphenylene-glutaric acid,[76] $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C(CO_2H)-CH_2-CH_2-CO_2H$, melts without gaseous evolution at 195-196°. At 260°, carbon dioxide is eliminated and an almost quantitative yield of γ-diphenylene-butyric acid is produced. Apparently, no anhydride is produced by this process, although a quantitative yield is reported when acetyl chloride is employed as a dehydrating agent. It will be recalled that diphenylene succinic acid formed an anhydride by heating in the normal manner. This fact emphasizes the greater ease of anhydride formation in the succinic series.

β,β-Dimethylpropane-tricarboxylic acid [77] melts at 172°, and forms an anhydride at 200°:



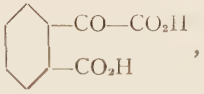
Curiously, diglycollic acid,[78] $O(CH_2-CO_2H)_2$, and methyl diglycollic acid [79] or dilactic acid and its homolog, $HO_2C-\underset{CH_3}{CH}-O-\underset{C_2H_5}{CH}-CO_2H$,

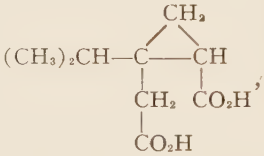
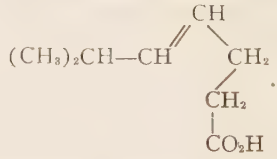
[73] Perkin, *J. Chem. Soc.* **81**, 256 (1902); Blaise and Courtot, *Compt. rend.* **139**, 292 (1904).
[74] Fichter and Merckens, *Ber.* **34**, 4176 (1901).
[75] Avery and Bouton, *Am. Chem. J.* **20**, 513 (1898).
[76] Wislicenus and Mocker, *Ber.* **46**, 2789 (1913).
[77] Thorpe and Wood, *J. Chem. Soc.* **103**, 1579 (1913).
[78] Anschütz, *Ann.* **259**, 187 (1890).
[79] Jungfleisch and Godchot, *Compt. rend.* **145**, 70 (1907).

none of which are glutaric acid types, also form cyclo-anhydrides when they are distilled. In these cases it will be noticed that the only difference, however, is the replacement of a methylene group by oxygen:

$$HO_2C{-}CHR{-}O{-}CHR{-}CO_2H \longrightarrow O{<}\begin{matrix}CHR{-}CO\\ \\ CHR{-}CO\end{matrix}{>}O + H_2O\,..$$

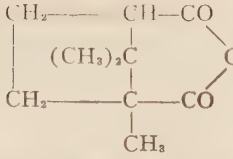
(R=H, or CH_3, or C_2H_5.)

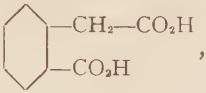
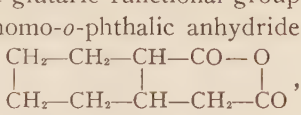
Although acetone dicarboxylic acid, $CO(CH_2CO_2H)_2$, is related to glutaric acid, it is also a β-ketonic acid. It is in keeping with the latter fact that pyrolysis [80] into acetone occurs at 135° (the melting point). α-Oximinoglutaric acid, $\begin{matrix}HO_2C{-}C{-}CH_2CH_2CO_2H\\ \|\\ NOH\end{matrix}$, is reported [81] to evolve carbon dioxide vigorously at its melting point, 152°. Very probably, the course of this pyrolysis is much more profound than simple decarboxylation would infer (for oximes, consult a later chapter). The pyrolysis of phthalonic acid,  , has already been discussed on p. 357; it does not yield an acid anhydride of the glutaric type.

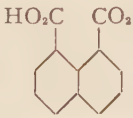
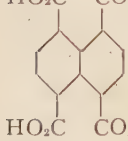
α-Tanacetogen-dicarboxylic acid,[82]  , illustrates one case where the functional group of glutaric acid is part of a cyclic system. It lacks the tendency to form an anhydride by heating. At 200-240°, it is reported to lose carbon dioxide and change into γ,δ-*iso*-octenic acid,  . If this correctly represents the change, the carboxyl originally attached to the cyclic nucleus is eliminated, following which rearrangement occurs. This one illustration which involves a cyclopropane ring is exceptional.

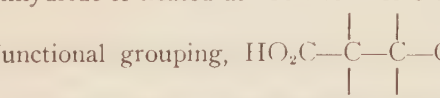
Normal behavior is again encountered in *d*-camphoric acid,[83] a derivative of cyclopentane. Above its melting point, 187°, it changes

[80] Pechmann, *Ann.* **261**, 158 (1890).
[81] Wolff, *Ann.* **260**, 112 (1890).
[82] Fromm and Lischke, *Ber.* **33**, 1192 (1900).
[83] Bouillon and Lagrange, *Ann. chim.* [1] **23**, 171 (1797); Malaguti, *Ann.* **22**, 41 (1837); Laurent, *Ann.* **22**, 138 (1837); Brühl and Braunschweig, *Ber.* **26**, 285 (1893).

into *d*-camphoric anhydride,  . If the acid is heated in a slow current of carbon dioxide until all the water has been removed, the anhydride may then be distilled in a more rapid current and at a higher temperature. The yield is nearly theoretical, and the preparation is a fairly rapid one.

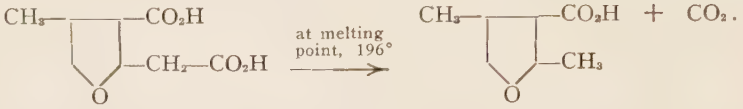
o-Carboxyphenylacetic acid,  , forms its anhydride [84] at 195° (melting point, 175°). *Ortho* carbon atoms in the benzene nucleus may, therefore, be incorporated in the glutaric functional group (see Bredt's rule). Quite closely related to homo-*o*-phthalic anhydride is *o*-carboxy*cyclo*hexane acetic anhydride,  , which occurs [18] in *cis* and *trans* modifications. An equilibrium mixture of 25 percent *cis* and 75 percent *trans* is produced by 10 hours' maintenance at 220°.

Naphthalic acid,  , forms its anhydride [85] with especial ease at 140-180°. In many reactions, *peri* substituents behave like *ortho* groupings. Thus, it might be anticipated that naphthalic acid would resemble phthalic acid in this respect. Similarly, the tetracarboxylic acid,  , behaves like pyromellitic acid, since it undergoes [86] pyrolysis into the dianhydride if heated at 130-140° for 5 hours.

When the functional grouping,  , is part of a **heterocyclic system**, thermal dehydration to the acid anhydride is not observed. Although *o*-carboxyl-phenylacetic acid, $HO_2C—C_6H_4—CH_2CO_2H$, forms its anhydride easily by heat, the furan analog,

[84] Graebe and Trümpy, *Ber.* **31**, 376 (1898).
[85] Behr and van Dorp, *Ann.* **172**, 263 (1874).
[86] Freund and Fleischer, *Ann.* **402**, 77 (1914); Bamberger and Philip, *Ann.* **240**, 186 (1887).

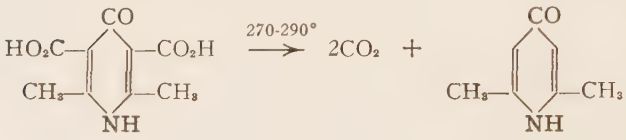
(4-methyl-3-carboxyfuryl-2)-acetic acid, merely becomes decarboxylated [87] to form an isomer of pyrotritaric acid:



In *N*-heterocyclic compounds, this condition also exists:

1-Phenylpyrazole-3,5-Dicarboxylic Acid [88] — *1-Phenylpyrazole-3-Carboxylic Acid*

4-Phenylpyrazole-3,5-Dicarboxylic Acid [89] — *4-Phenylpyrazole*



Lutidone Dicarboxylic Acid [90] — *Lutidone*

Reference has already been made (p. 413) to the decomposition of thiophene-2,4-dicarboxylic acid. In sulfone-diacetic acid,[91] the two carboxyls are separated by a chain of three atoms, but the acid anhydride is not produced by heating. At 200°, it changes into dimethyl sulfone:

$$SO_2(CH_2CO_2H)_2 \longrightarrow SO_2(CH_3)_2 + 2CO_2.$$

Since the very negative —SO_2— group is attached to the α-carbon, the acid structurally resembles malonic acid more than glutaric. Loss of the carboxyls would, therefore, be anticipated (see p. 337).

[87] Feist, *Ber.* **35**, 1549 (1902).
[88] Claisen and Roosen, *Ann.* **278**, 286, 294 (1893).
[89] von Pechman and Burkard, *Ber.* **33**, 3596 (1900).
[90] Conrad and Guthzeit, *Ber.* **20**, 156 (1887).
[91] Lovén, *Ber.* **17**, 2819 (1884).

Other Dicarboxylic Acids.

It will be recalled (p. 14) that Blanc's rule dealt with cyclic ketone formation from acids, such as $HO_2C—(\overset{|}{C})_{4\ or\ 5}—CO_2H$, related to adipic or pimelic acids. Blanc [92] heated adipic acid to 215-240° in the presence of acetic anhydride, and formed adipic anhydride. The excess of acetic acid was then distilled away, and the residual adipic anhydride was subjected to thermal decomposition. Carbon dioxide was eliminated and cyclopentanone was produced in about 50 percent yield:

$$(CH_2)_4\begin{matrix}CO\\<\ >O\\CO\end{matrix} \longrightarrow \begin{matrix}CH_2—CH_2\\|\qquad\quad>CO\\CH_2—CH_2\end{matrix} + CO_2.$$

Similarly, Blanc prepared cyclohexanone from pimelic anhydride, after first preparing the latter from pimelic acid with acetic anhydride. The catalytic effect [93] of manganous oxide (80 percent yield at 350°) was demonstrated with adipic acid by Sabatier and Mailhe. At 500°, without the catalyst, their reported yield of cyclopentanone was 20 percent.

Adipic acid distils [11] without decomposition, and does not give the anhydride in this way. So also, β- or γ-methylpimelic acids [94] distil undecomposed. In most of the cases related to pimelic and adipic acids, the thermal decomposition is from the acid anhydride to the cyclic ketone. The step from the acid to the acid anhydride is usually formed chemically with the aid of acetic anhydride. Blanc mentioned that by this method, substituted pentanones and substituted hexanones could be prepared from the substituted adipic or pimelic acids in yields approaching the theoretical. Another synthesis of this type is that of δ-ketohexahydrobenzoic acid [95] from pentane-$\alpha,\gamma,\varepsilon$-tricarboxylic acid; yield, 7 grams (crude) from 15 grams.

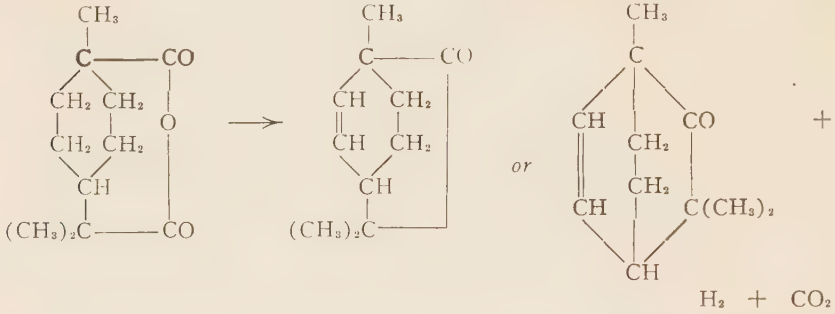
$$HO_2C—CH(CH_2CH_2CO_2H)_2 \xrightarrow{Ac_2O} HO_2C—CH(CH_2CH_2CO)_2O \xrightarrow[\text{and 15 mm.}]{200\text{-}220°}$$

$$\begin{matrix}&&CH_2—CH_2\\&\diagup&&\diagdown\\HO_2C—CH&&&&CO.\\&\diagdown&&\diagup\\&&CH_2—CH_2\end{matrix}$$

Barbier and Grignard [96] report an interesting synthesis of a bicyclic ketone, by distilling the anhydride of *cis*-menthane-1,8-dicarboxylic acid

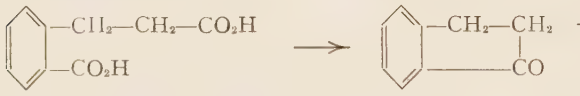
[92] Blanc, *Compt. rend.* **144**, 1356 (1907).
[93] Sabatier and Mailhe, *Compt. rend.* 158, 985 (1914).
[94] Einhorn and Ehret, *Ann.* **295**, 180 (1897).
[95] Perkin, Jr., *J. Chem. Soc.* **85**, 424 (1904).
[96] Barbier and Grignard, *Compt. rend.* **145**, 255 (1907).

at atmospheric pressure (250-350°). The anhydride was previously produced from the acid by heating with acetic anhydride.

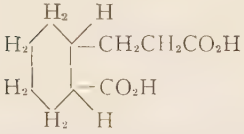


The loss of hydrogen in this process resembles the dehydrogenation of terpenes into cymene by thermal means.

Hydrocinnamic-*o*-carboxylic acid yields [97] hydrindone when it is distilled in a vacuum:

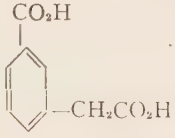


In this case, acetic anhydride appears to be unnecessary. However, neither the *cis-* nor the *trans-o*-carboxy-*cyclo*-hexanepropionic acid,



, is changed [98] into an aliphatic ketone containing one less carbon atom when heated alone, but evaporation of either one to 140° with acetic anhydrides followed by distillation at 240-260° yields hexahydro-α-hydrindone, $C_6H_{10}<\begin{matrix}CH_2\\ \\ CO\end{matrix}>CH_2$. In the absence of the acetic anhydride, the *cis* acid rearranges into the *trans* form at 250°, and the latter distils unchanged.

Although hydrocinnamic-*o*-carboxylic acid behaves like adipic acid, because of Bredt's rule this behavior would not be anticipated for the *meta* and *para* analogs,

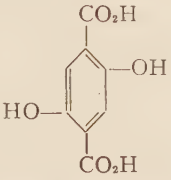
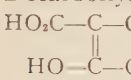


or

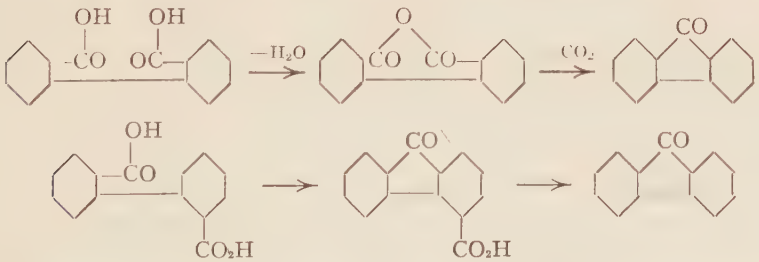
, even though they

[97] König, *Ann.* **275**, 341 (1893).
[98] Windaus, Huckel and Reverey, *Ber.* **56**, 91 (1923).

possess the functional group, $HO_2C—(C)_4—CO_2H$. The corresponding hexahydro compounds would not be open to the objection of Bredt's rule, and they should behave normally.

Dry distillation[99] of dihydroxyterephthalic acid,  , gives hydroquinone, the reaction being merely one of decarboxylation. The yields are only fair. This acid is related not only to adipic acid but it also possesses the functional group of the β-ketonic acids (enol form). Decarboxylation would also be anticipated in succinylosuccinic acid,  (or its keto formula), and this actually[100] occurs at 200°. Diacetyl-dicarboxylic acid,[101] $(—CO—CH_2—CO_2H)_2$, decomposes readily into diacetyl. This is also a β-ketonic acid.

Diphenic acid also possesses four carbon atoms between its two carboxyls. Distillation of this acid[102] gives a mixture of compounds from which diphenic anhydride and *o*-diphenylene-ketone-carboxylic acid may be isolated. Both of these compounds are dehydration products of diphenic acid. The yield of the former may be materially increased by the use of acetic anhydride, whereas the latter is best formed in the presence of sulfuric acid. At the temperature of boiling sulfur, both of these compounds lose carbon dioxide completely to form diphenylene ketone or fluorenone. The following equations indicate these changes.

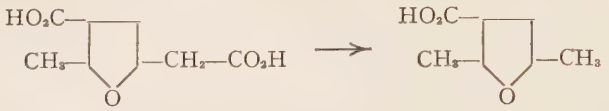


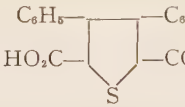
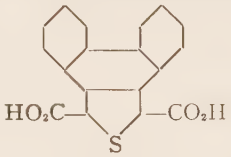
In **heterocyclic systems** related to adipic acid, the general behavior at elevated temperatures is not cyclic ketone formation. Simple decarboxylation is quite generally the rule in the cases which have been

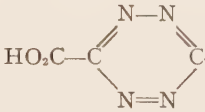
[99] Herrmann, *Ann.* **211**, 327 (1882).
[100] Herrmann, *ibid.* p. 321.
[101] Fittig, Daimler and Keller, *Ber.* **20**, 3184 (1887).
[102] Graebe and Mensching, *Ber.* **13**, 1302 (1880); Graebe and Aubin, *Ann.* **247**, 265 (1888).

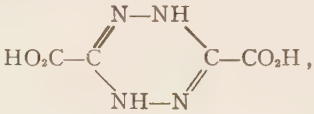
studied. In this respect, these compounds behave like the corresponding ones in the succinic or glutaric series.

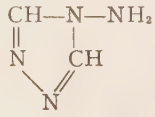
Methronic acid, for example, gives pyrotritaric acid [103] when it is distilled:



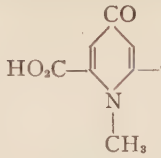
See p. 413 for a similar preparation of pyrotritaric acid. Dehydromucic acid, , yields both furoic acid and furan,[104] but the thiophene analog sublimes at 350° without decomposition. However, 3,4-diphenyl-thiophene-2,5-dicarboxylic acid,  , pyrolyzes at 300°, leaving a residue of 3,4-diphenylthiophene.[105] Phenanthro-*iso*thiophene-dicarboxylic acid,  , leaves nearly pure phenanthro*iso*thiophene as a residue when it is heated in a free flame; the decomposition point is 270°.

Tetrazine dicarboxylic acid,  , undergoes pyrolysis [106] into tetrazine at 148°. The dihydro compound,



is gradually transformed into *N*-aminotriazole,  , at 100°. At 150°, the evolution of carbon dioxide is very rapid. The decompo-

[103] Fittig and von Eynern, *Ann.* **250**, 182, 190 (1888).
[104] Heinzelmann, *Ann.* **193**, 192 (1878); Sohst and Tollens, *Ann.* **245**, 21 (1888).
[105] Hinsberg, *Ber.* **43**, 902 (1910).
[106] Curtius and Lang, *J. prakt. Chem.* [2] **38**, 557 (1888); Hantzsch and Lehmann, *Ber.* **33**, 3669 (1900); Curtius, Darapsky and Müller, *Ber.* **39**, 3415 (1906).

sition of chelidamic acid has already been mentioned (p. 378); its *N*-methyl derivative,  , loses carbon dioxide [107] at 180° with the production of *N*-methyl-γ-pyridone.

Very little is known of the pyrolysis of *higher dicarboxylic acids*. Suberic or azelaic acids, $HO_2C—(CH_2)_n—CO_2H$ ($n = 6$ or 7), are changed,[108] in part, to their anhydrides by distillation. Although suberic acid can be changed into suberone [92] by distillation with acetic anhydride, the yields are very poor. Tetradecane-1,14-dicarboxylic acid is reported [109] to yield cyclopentadecanone when heated.

[107] Haitinger and Lieben, *Monatsh.* **6**, 307 (1885).
[108] Anderlini, *Gazz. chim. ital.* **24**, I, 475 (1894); *Atti accad. Lincei* [5] **3**, I, 394 (1894).
[109] Naef et Cie, Brit. 235,540, June 16, 1924; *Chem. Abstracts* **20**, 917 (1926).

CHAPTER 15.

HYDROXY ACIDS AND AMINO ACIDS.

Hydroxy Acids.

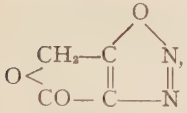
The presence of two reactive groups in *hydroxy acids,* namely, hydroxyl and carboxyl, makes these compounds interesting from the standpoint of pyrolysis. In general, the distance of these groups from each other determines the course of the decomposition. The simple α-hydroxy acids become dehydrated to glycollides or lactides, whereas the higher homologs may decompose further with loss of carbon monoxide. Furthermore, more complex α-hydroxy acids may become dehydrated to unsaturated acids, thus simulating the change encountered with the β-hydroxy acids. γ- or δ-Hydroxy acids change into lactones. In all of these cases, the elements of water are eliminated.

α-Hydroxy Acids.

Glycollic Acid. Glycollic acid forms three distinct products of dehydration, depending on the vigor of heating. Ordinary glycollide, $\begin{matrix} CH_2—O—CO \\ | \quad\quad | \\ CO—O—CH_2 \end{matrix}$, is produced when glycollic acid [1] is distilled in a vacuum. The fact that this compound is an ester suggests that another dehydration product of glycollic acid, $(2C_2H_4O_3 — H_2O)$, which is formed by long heating at 100° on the water bath is also an ester with the formula, $CH_2OH—CO—O—CH_2—CO_2H$, but such seems not to be the case. In the latest volume of Beilstein,[2] an anhydride formula, $(CH_2OH—CO)_2O$, is given but it is questioned. It seems exceedingly doubtful that the anhydride formula is correct, since anhydrides of other monocarboxylic acids are never formed so simply. The fact that this substance melts at 128-130° has been taken as sufficient evidence that it cannot be glycollyl-glycollic acid, inasmuch as this compound is reported to melt at 99-100°. Wolff and Lüttringhaus [3] prepared the latter substance from diazotetronic anhydride by the hydrolytic action of cold

[1] Drechsel, *Ann.* **127**, 154 (1863); Fittig and Thomson, *Ann.* **200**, 79 (1879); Fahlberg, *J. prakt. Chem.* [2] **7**, 336 (1873).
[2] Beilstein's "Handbuch der Organischen Chemie," 4th edition, **3**, 239.
[3] Wolff and Lüttringhaus, *Ann.* **312**, 146 (1900).

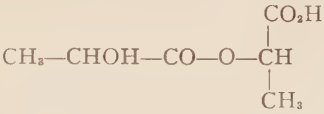
barium hydroxide. The structure assigned to diazotetronic anhydride,

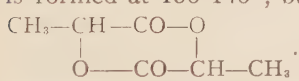


its hydrolysis. From the evidence at hand, it seems that there is even less proof for the material melting at 99° than for the material which melts at 128°. Both substances react with water to give glycollic acid.

A polymer of glycollide is formed when glycollic acid or glycollide is heated at 240-280°. The polymer melts at 223°, and becomes depolymerized by vacuum distillation.

Lactic Acid. Lactide is the most common thermal dehydration product of lactic acid, resulting as it does from the distillation of the acid. It is probably present [5] in most samples of the acid. "Lactic acid anhydride", presumably an ester, lactyl lactic acid,



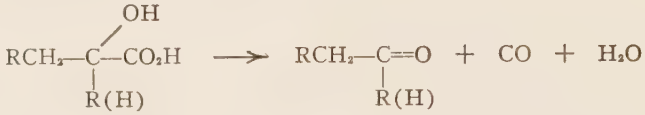
is formed at 130-140°, but it is undoubtedly contaminated with lactide,  . Lactide [6] is prepared at 150°; it distils undecomposed at 255°. If lactic acid is heated a few hours at 90-100° and 25 mm. pressure, the presence of a third dehydration product, trilactic acid, can be demonstrated.[7] This distils at about 250° (diminished pressure) after lactide has been first distilled from the mixture. Trilactic acid has the formula,

Nef investigated the behavior of lactic acid [8] when it was passed at 440-460° over pumice. About 75 grams of the acid (73.3 percent strength) was passed through the tube in 3 hours. In the 47.3 grams of distillate, 22 grams of water and 4.5 grams of acetaldehyde were identified. Alcohol was practically absent, and neither was ethylene formed. The gaseous products of the pyrolysis, freed from carbon dioxide, were seven liters in volume. This indicates at least a partial breakdown of lactic acid into acetaldehyde, carbon monoxide and water.

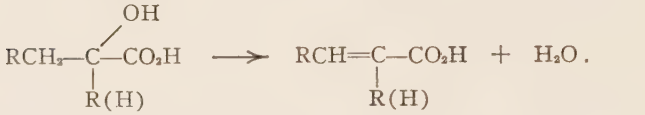
[4] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Berlin and Leipzig, Walter de Gruyter Co., **2**, III, 624.
[5] Krafft and Dyes, *Ber.* **28**, 2591 (1895); Krauskopf and Carter, *J. Am. Chem. Soc.* **48**, 1476 (1926).
[6] Engelhardt *Ann.* **70**, 244 (1849); Henry, *Ber.* **7**, 755 (1874).
[7] Jungfleisch and Godchot, *Compt. rend.* **140**, 502 (1905).
[8] Nef, *Ann.* **335**, 298 (1904).

When α-hydroxybutyric acid is distilled (225°) at ordinary pressure, some type of anhydride [9] is produced. α-Hydroxy*iso*valeric acid and α-hydroxy*iso*caproic acid [10] change also to lactide-like anhydrides on heating.

Two other types of decomposition are encountered in α-hydroxy acids, and these types become increasingly important in the more complex acids. α-Hydroxy acids may change into aldehydes or ketones, or they may yield unsaturated acids in accordance with the general reactions:



or



It was Blaise [11] who pointed out that aldehydes could be prepared in good yields (50-60 percent) by the distillation of lactides, and it is reasonable to infer that the loss of carbon monoxide, as shown in the above equation, is more properly a function of the lactide than of the α-hydroxy acid. As Blaise noted, this reaction affords a means of degrading the fatty acids. The essential steps are:

(1) Preparation of the α-bromo acid, and from it
(2) Preparation of the α-hydroxy acid.
(3) Pyrolysis of the latter into the lactide, and distillation of the lactide. The aldehyde which is thus produced contains one less carbon atom than the original acid.
(4) Oxidation of the aldehyde to the acid. This process was carried out with hexoic, pelargonic, lauric, myristic and palmitic acids.

α-Hydroxy-heptoic acid, by this method,[12] changes into caproic aldehyde in 50 percent yield, but in addition it yields butyl ethylene, an unsaturated acid (possibly heptenoic acid), and α-hydroxyheptolactide, $CH_3-(CH_2)_4-CH(-O-CO-)-CO-O-CH(-(CH_2)_4-CH_3)-$. This lactide cannot be isolated unless the pyrolysis is stopped at an early stage, since at 280-300° it decomposes into the aldehyde and carbon monoxide, leaving a residue

[9] Naumann, *Ann.* **61**, 119 (1861); Markownikoff, *Ann.* **153**, 245 (1870).
[10] Guthzeit, *Ann.* **209**, 240 (1881); Schmidt and Sachtleben, *Ann.* **193**, 113 (1878).
[11] Blaise, *Compt. rend.* **138**, 697 (1904).
[12] Bagard, *Bull. soc. chim.* [4] **1**, 307 (1907).

of polylactide. Considerably better yields of caproic aldehyde are formed from the pyrolysis of α-acetoxyheptoic acid, $CH_3-(CH_2)_4-CH<^{O-COCH_3}_{CO_2H}$, A 68.7 percent yield of aldehyde was reported.

Bagard obtained 71 percent of nonaldehyde as a result of the distillation of α-hydroxycapric acid. Carbon monoxide was obtained in quantity, as well as a small amount of the aldehyde polymer, and an unsaturated acid. From α-hydroxyundecoic acid, he obtained 52 percent of capric aldehyde, some of its polymer, carbon monoxide, carbon dioxide, and small amounts of decene-1. α-Hydroxy-β-ethyl-nonoic acid behaved similarly, yielding α-ethyl caprylic aldehyde and considerable quantities of an olefine which was thought to be ethyl-2-octene-1. These olefines, of course, are the result of the decarboxylation of the α,β-unsaturated acids. As will be seen later, disubstituted glycollic acids tend to give these unsaturated acids more than the monosubstituted ones.

A good way to prepare pentadecyl aldehyde [13] is to heat α-hydroxypalmitic acid to 170° at 20-25 mm.:

$$CH_3(CH_2)_{13}-CHOH-CO_2H \longrightarrow CO + H_2O + CH_3(CH_2)_{13}-CHO.$$

Margaric aldehyde (50-60 percent yield), and some α-hydroxystearic acid lactide, $C_{16}H_{33}-CH(-O-CO)-CO-O-CH-C_{16}H_{33}$, are the result [14] of maintaining α-hydroxystearic acid at 270° for an hour. The mechanism for this transformation into the aldehyde was thought to proceed not only through the lactide, but also directly from the hydroxy acid:

$$CH_3(CH_2)_{15}-CHOH-CO_2H \longrightarrow CH_3(CH_2)_{15}-CHO + [HCO_2H]$$
$$[HCO_2H] \longrightarrow H_2O + CO.$$

In support of this is the fact that the lactide fails to decompose below 260°, and its pyrolysis is very slow at 270-280°; yet about 50 percent yields of margaric aldehyde result from the pyrolysis of the acid at 240-250°.

Similarly,[15] dry distillation of α,α′-dihydroxysebacic acid produces the aldehyde related to suberic acid:

$$HO_2C-CHOH-(CH_2)_6-CHOH-CO_2H \longrightarrow H-CO-(CH_2)_6-CHO + 2CO + 2H_2O.$$

The yields in this case are small, but they can be made very satisfactory by heating the diacetyl derivative of the dihydroxy acid instead of the acid itself. To produce this effect in compounds like lactic acid, or other

[13] St. Landa, *Chem. Listy* **19**, 264 (1925); *Chem. Abstracts* **19**, 3251 (1925).
[14] LeSueur, *J. Chem. Soc.* **85**, 827 (1904); **87**, 1888 (1905).
[15] LeSueur, *ibid.* **91**, 1365 (1907).

monosubstituted glycollic acids of low molecular weight, it is necessary to distil the acid in the presence of hydrochloric acid or of sulfuric acid.

Aromatic Substituents in Glycollic Acid Nucleus. Aromatic substituents in the glycollic acid nucleus appear to exert a predominating influence in the thermal decomposition of such compounds. Mandelic acid, with one phenyl group, gives diphenyl-maleic anhydride as well as benzaldehyde. Benzilic acid, with two phenyl groups, changes into diphenyl ketene and benzophenone. Both of these products may be traced through an intermediate "ether acid-anhydride", $O<\begin{matrix}CR_2—CO\\ \\ CR_2—CO\end{matrix}>O$, which is isomeric with the lactide, or "inner ester", type of compound. The reaction has been studied in considerable detail with mandelic acid and benzilic acid.

To gain an insight into the reason why the reaction mechanism of these aryl hydroxy acids differs from the alkyl hydroxy acids, it is helpful to recall the contrasting modes of pyrolysis of ethyl alcohol, benzyl alcohol and benzohydrol (pp. 149, 156 and 160). Ethyl alcohol never yields diethyl ether, whereas benzyl alcohol and benzohydrol, respectively, do yield dibenzyl ether and di-benzohydryl ether. By analogy, therefore, since $CH_3—CH_2OH$ does not give $(CH_3CH_2)_2O$, then $\begin{matrix}CH_3—CHOH\\ \\ CO_2H\end{matrix}$ should not give $\left(\begin{matrix}CH_3—CH—\\ \\ CO_2H\end{matrix}\right)_2O$; also, since $C_6H_5—CH_2OH$ yields $(C_6H_5CH_2)_2O$, then $\begin{matrix}C_6H_5—CH—OH\\ \\ CO_2H\end{matrix}$ should yield $\left(\begin{matrix}C_6H_5—CH—\\ \\ CO_2H\end{matrix}\right)_2O$; and finally, since $(C_6H_5)_2CHOH$ yields $((C_6H_5)_2CH)_2O$, then $\begin{matrix}(C_6H_5)_2C—OH\\ \\ CO_2H\end{matrix}$ should yield $\left(\begin{matrix}(C_6H_5)_2C——\\ \\ CO_2H\end{matrix}\right)_2O$.

What, now, are the facts regarding mandelic acid? First of all, active mandelic acid [16] is racemized at 160°, and *i*-mandelic acid undergoes a curious change [17] in its melting point when it is maintained at 130° for several hours, dropping from 118° to 106°, a value which it retains even after recrystallization from benzene.

Secondly, when mandelic acid is heated at 200-205°, benzaldehyde is evolved. The residue, after distillation of all the aldehyde, gives analytical values [18] for a mixture of dehydration products of mandelic acid. The formulas for the lactide, $\begin{matrix}C_6H_5CH—CO—O\\ \\ O——CO—CH—C_6H_5\end{matrix}$, and for the

[16] Lewkowitsch, *Ber.* **16**, 2721 (1883).
[17] Kizhner, *J. Russ. Phys. Chem. Soc.* **56**, 15 (1925); *Chem. Abstracts* **19**, 2940 (1925).
[18] Bischoff and Walden, *Ann.* **279**, 118 (1894).

ester, $C_6H_5CHOH—CO—O—CH(C_6H_5)—CO_2H$, were suggested as possible compounds, but in the absence of evidence to the contrary, it seems equally reasonable to assume the "ether acid-anhydride" formula, $O<^{C_6H_5—CH—CO}_{C_6H_5—CH—CO}>O$. As will be shown shortly, such an intermediate compound would explain very neatly other facts which are observed, and which would be impossible of explanation through the lactide structure. In fact, there is evidence which very clearly supports it, namely, the conversion into diphenyl maleic anhydride in about 50 percent yields. This occurs when mandelic acid is gradually heated from 100° to 190° under diminished pressure (500 mm. at the outset, to 40-60 mm. after the gas evolution ceases). Other products are benzaldehyde and a gas which was stated to be carbon monoxide. There is nothing in the context of Bischoff and Walden's article to show that they have positively identified any of the gaseous products. Carbon dioxide would be anticipated as a primary decomposition product from the "ether acid-anhydride" formula, and carbon monoxide as a secondary decomposition product, due to the breakdown of phenyl ketene. Carbon monoxide should be a primary decomposition of the "lactide". Assuming the correctness of the "ether acid-anhydride" in preference to the "lactide", the steps in the decomposition of mandelic acid are as follows:

$$2C_6H_5CH(OH)—CO_2H \longrightarrow H_2O + \left[O<^{C_6H_5—CH—CO}_{C_6H_5—CH—CO}>O\right]$$

$$\left[O<^{C_6H_5—CH—CO}_{C_6H_5—CH—CO}>O\right] \nearrow \; 2H_2O + C_6H_5—C(=CO)—C(=CO)—C_6H_5$$

$$\left[O<^{C_6H_5—CH—CO}_{C_6H_5—CH—CO}>O\right] \searrow \; C_6H_5CHO + CO_2 + [C_6H_5CH=C=O]$$

In criticism of the proposed mechanism, it may be pointed out that this presents a definite case wherein a *monocarboxylic* acid seemingly becomes dehydrated to an acid anhydride. Although this is quite customary for *dicarboxylic* acids of the succinic and glutaric type, it is indeed rare for a monocarboxylic acid to change into its anhydride at as low a temperature as 100-150° or even 200°. It will be recalled, however, that diglycollic acid (p. 415) and related compounds possessing the structure, $O(CHR—CO_2H)_2$, become dehydrated to the acid anhydride, $O(CHR—CO)_2O$, by distillation. It is reasonable to assume, therefore, that the first step in the pyrolysis of mandelic acid is the formation of a "dimandelic acid", $O(C(C_6H_5)_2—CO_2H)_2$. This, being no longer a monocarboxylic acid, can then form a 6-membered cyclic anhydride by further heating. Precisely this type of mechanism will be

put forward to explain the facts of pyrolysis regarding benzilic acid and other aryl α-hydroxy acids.

The third fact regarding the pyrolysis of mandelic acid is that phenyl acetic acid is one of the reaction products, at least when the temperature is maintained at 250°. The mechanism which has been proposed accounts very creditably for the known products of the reaction, such as diphenyl maleic anhydride, benzaldehyde and gases, but it also infers that phenyl ketene should be one of the reaction products. In an effort to isolate it, Staudinger [19] obtained only an amorphous product. The fact that water is one of the products of the reaction makes it seem plausible that phenyl ketene should be a precursor of phenylacetic acid:

$$C_6H_5CH{=}C{=}O + H_2O \longrightarrow C_6H_5CH_2{-}CO{-}OH.$$

The isolation of phenylacetic acid as a reaction product, therefore, would be excellent proof of the transitory existence of phenyl ketene.

The author [20] has recently proven that phenylacetic acid is readily identified as a thermal decomposition product of mandelic acid. By heating 8 grams (0.052 mol) of mandelic acid in a slow current of nitrogen for 1.5 hours at 250°, the following products were identified:

1. Volatile portion; carbon dioxide (absorbed in Geissler bulb), 0.0157 mol; benzaldehyde, 0.0198 mol; water, about 0.01 mol.
2. Residue in flask; unchanged mandelic acid, 0.010 mol, and phenylacetic acid, 0.011 mol.

The phenylacetic acid was isolated from the mandelic acid by vacuum distillation, and then purified by crystallization, and its identity confirmed by the method of mixed melting points. For 0.042 mol of decomposed mandelic acid, the equation would demand 0.021 mol each of benzaldehyde, carbon dioxide and phenylacetic acid if the reaction went to completion. The yield of phenylacetic acid is, therefore, over 50 percent of the theoretical.

Systematic experiments with symmetrical trimethyl mandelic acid have not been performed. However, it has been established [21] that the chief product from its dry-distillation is mesityl acetic acid:

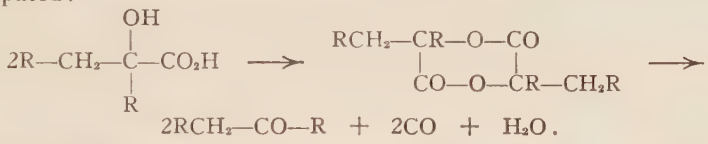
$$2,4,6\text{-}(CH_3)_3C_6H_2{-}CHOH{-}CO_2H \longrightarrow (CH_3)_3C_6H_2{-}CH_2{-}CO_2H.$$

Much water is formed, and there is considerable charring. If one assumed an "ether acid-anhydride" as an intermediate compound, its breakdown to a transient ketene, $(CH_3)_3C_6H_2{-}CH{=}CO$, would be

[19] Staudinger, *Ber.* **44**, 545 (1911).
[20] Hurd and Smith, unpublished results.
[21] Meyer and Molz, *Ber.* **30**, 1276 (1897).

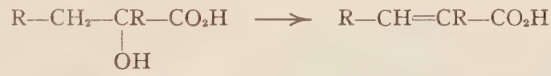
anticipated, which, with water, would give mesityl acetic acid. Meyer and Molz suggested no such mechanism for this change. They demonstrated that the quantity of mesitylene carboxylic acid, $(CH_3)_3C_6H_2—CO_2H$, in the reaction mixture was negligible.

Disubstituted Glycollic Acids. When the hydroxyl group of an α-hydroxy acid is attached to a tertiary carbon atom, it has been shown that lactide formation with the eventual production of ketones may be anticipated:

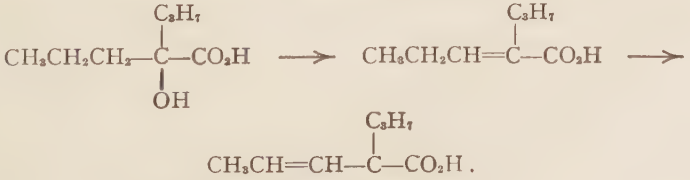


$$2RCH_2—CO—R + 2CO + H_2O.$$

Frequently, however, this reaction assumes a minor part because of the greater tendency for the production of α,β-unsaturated acids:

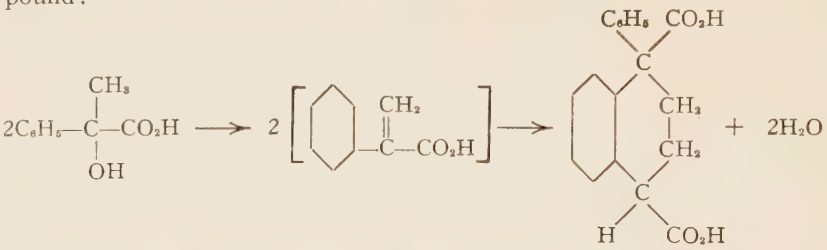


Thus, when dimethyl glycollic acid,[22] $(CH_3)_2C<^{CO_2H}_{OH}$, is distilled (about 212°), some of the lactide is produced, but about one-third of the acid is changed into methacrylic acid, $CH_2=C(CH_3)—CO_2H$, and about one-half (48 percent) into acetone. The experience with diethyl glycollic acid, $(C_2H_5)_2C<^{OH}_{CO_2H}$, which gives only a 5 percent yield of diethyl ketone, shows that the yield of ketone decreases as the molecular weight of the disubstituted glycollic acid increases. Conversely, the amount of unsaturated acid increases under these circumstances. Diethyl glycollic acid also gives a lactide, but in the higher homologs of this series, lactides are no longer observed. If the unsaturated acid exists in two forms, it is the labile form that appears to predominate in these pyrolyses. This is particularly true in the case of diethyl glycollic acid. A wandering of the double bond has been observed in the higher members. Some β,γ-unsaturated acid is formed as a result of the distillation of di-*n*-propyl-glycollic acid, indicating the following steps:



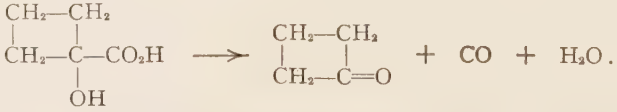
[22] Blaise and Bagard, *Compt. rend.* **142**, 1087 (1906).

Atrolactic acid, $C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO_2H$, furnishes [23] an example in which polymerization follows the formation of the simple unsaturated acid. If anhydrous atrolactic acid is heated for 30 hours at 140-160° in an atmosphere of carbon dioxide, it is smoothly converted into *α-iso*atropic acid, and this constitutes the best method of synthesis for this compound:



At 200°, a mixture of *α*- and *β*-isomers (33 percent beta) is produced. These are probably *cis-trans* isomers.

The preparation of ketones from *α*-hydroxy acids gives poor yields as has been shown, because of competing reactions. Frequently, as in the case of cyclobutanone, it is a convenient method of synthesis in spite of this fact. The yield of cyclobutanone [24] from 1-hydroxy-cyclobutane-1-carboxylic acid, by distillation of the latter at 280-300°, is 15 percent.



Over 700 cc. of gases were collected when 10 grams of the *α*-hydroxy acid was used. This gas analyzed 90 percent carbon monoxide and 10 percent carbon dioxide. A crystalline anhydride, $C_{10}H_{12}O_4$, and other non-crystalline anhydrides remained as the residue when the original hydroxy acid was distilled at 8-10 mm. These anhydrides failed to regenerate the parent acid when heated with water at 120°, but they decomposed into cyclobutanone and carbon dioxide when heated alone. Whether or not the $C_{10}H_{12}O_4$ compound was the lactide $\begin{matrix}(CH_2)_3{=}C{-}O{-}CO\\ \quad\quad\quad\

perimental data, particularly its non-hydrolysis and its pyrolysis into carbon dioxide (as well as carbon monoxide), point to the "ether acid-anhydride" type of compound, $\begin{matrix}(CH_2)_3{=}C{-}CO\\ O< \quad >O\\ (CH_2)_3{=}C{-}CO\end{matrix}$.

Diaryl-glycollic Acids. For several reasons, a study of the pyrolysis of benzilic acid has been of considerable importance. Nef [25] was interested in its behavior because it appeared to offer a good vehicle for the chemistry of bivalent carbon. When maintained (15 grams) at 180-200° for 20-30 minutes, he demonstrated the presence of diphenyl-acetic acid (5 grams), benzophenone (about 4 grams), carbon dioxide (1.18 grams), water, and varying amounts of a red resin, and the complete absence of carbon monoxide. Nef's interpretation of these facts, which has been proven to be inadequate, hinged on the existence of a transient diphenylmethylene:

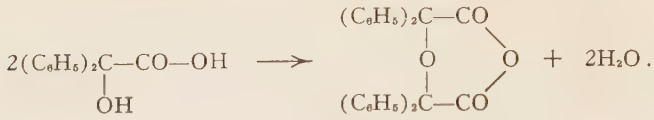
$$\begin{matrix}(C_6H_5)_2C<^{OH}_{CO_2H} & \longrightarrow & [(C_6H_5)_2C] + H_2O + CO_2\\ \downarrow 2[H] & & \downarrow H_2O\\ (C_6H_5)_2CH{-}CO_2H + H_2O & & (C_6H_5)_2CO + 2[H]\end{matrix}$$

Several years earlier, benzophenone had been identified [26] as a product of decomposition of benzilic acid at 180°. These investigators also prepared benzilide, a compound which was shown by Staudinger [27] to be formed in good yields (16 grams from 20 grams) when benzilic acid was maintained at 100° for one week. Nearly as good yields are obtained, and far less time consumed, in its preparation at 155-165° in a vacuum of 15 mm. This work is of more than ordinary interest, since it was shown [28] by Stollé that benzilide does not possess the customary inner-ester formula, but is instead an "ether acid-anhydride". Stollé's conclusion is based upon the fact that benzilide is formed by the interaction of diphenyl-chloroacetic anhydride with mercuric oxide:

$$((C_6H_5)_2CCl{-}CO)_2O \xrightarrow{HgO} \begin{matrix}(C_6H_5)_2C{-}CO\\ \quad | \quad \diagdown\\ \quad O \quad\ O\\ \quad | \quad \diagup\\ (C_6H_5)_2C{-}CO\end{matrix}$$

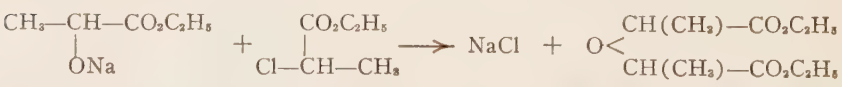
This makes it apparent, therefore, that in benzilic acid, it is easier for the two alcoholic hydroxyls, in two mols of the acid, to react with each other and form an ether than to react with the carboxyls and form an ester:

[25] Nef, *Ann.* **298**, 242 (1897).
[26] Klinger and Standke, *Ber.* **22**, 1213 (1889).
[27] Staudinger, *Ber.* **44**, 543 (1911).
[28] Stollé, *Ber.* **43**, 2473 (1910).



Other features concerning this reaction have already been expounded with mandelic acid. It is particularly interesting to point out again that benzohydrol, which has the grouping $(C_6H_5)_2C(OH)$— in common with benzilic acid, also gives its ether when heated. Concerning the formation of benzilide from diphenyl-ketene-oxide polymers, see p. 753.

Before dismissing the subject, it may be pointed out that these pyrolyses of mono- and di-aryl glycollic acids into an "ether acid-anhydride" should not be taken as a criterion for the behavior of mono- or di-alkylated glycollic acids, any more than the pyrolysis of benzohydrol should be taken as a criterion for the behavior of ethyl alcohol. The ester-like dehydration products of the alkyl glycollic acids seem to represent the facts correctly, although there may undoubtedly be transition types in which both the lactide and the ether acid-anhydride forms are produced. That the structures assigned to glycollide and lactide are correct is borne out not only by the fact that they regenerate the α-hydroxy acids on treatment with water, but also by the fact that they are formed when sodium salts of the α-bromoacids, R—$CHBr$—CO_2Na, are dry-distilled. Furthermore, lactide changes into lactamide when it is treated with dry ammonia, just as any ester would change into an amide. Dilactylic anhydride, $O<^{CH(CH_3)—CO}_{CH(CH_3)—CO}>O$, which differs from lactide, has been synthesized by a method that leaves no doubt as to its structure [29] by the following series of reactions:

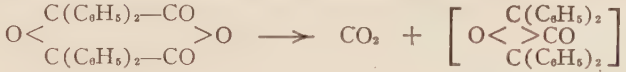


The ester thus formed is hydrolyzed to the corresponding dibasic acid, and it is changed into dilactylic anhydride by the action of heat or of acetyl chloride.

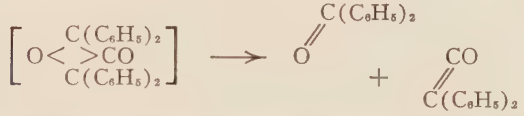
Benzilic acid changes into benzilide, as stated above, but other decomposition products appear if the heating is continued at a more elevated temperature. No appreciable decomposition of benzilide is apparent below 250°, but at its boiling point [30] it evolves 80.6 percent of the theoretical amount of carbon dioxide. Benzophenone, diphenyl

[29] Jungfleisch and Godchot, *Compt. rend.* **144**, 979 (1907); **145**, 72 (1907).
[30] Staudinger, *Ber.* **44**, 545 (1911).

ketene and some undecomposed benzilide [31] appear in the distillate. To account for this change, Staudinger assumed the following steps:



Then,

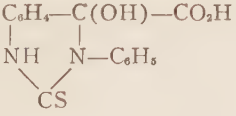


The presence of diphenyl ketene was confirmed by its conversion into diphenylacetic acid by the addition of water. Furthermore, if benzilic acid, instead of benzilide, is heated, diphenylacetic acid is invariably produced. Nef demonstrated this (p. 433), and Staudinger isolated 1.3 grams of it from 23.1 grams of benzilic acid when the latter was heated at 155-165° and 15 mm. for 12 hours. The chief product was 15.4 grams of benzilide.

The fact that diphenyl ketene is formed from benzilide is very reasonably interpreted from the ether acid-anhydride structure, whereas it would have been awkward indeed from the older lactide structure. Staudinger indicated that dimethoxybenzilic acid should behave analogously and such was found to be the case.

Many years ago, it was reported [32] that diphenylene glycollic acid, C_6H_4 | C_6H_4 >C< OH / CO_2H, undergoes pyrolysis above its melting point, 162°, with the evolution of water, carbon dioxide, and a resinous body which was insoluble in alkali, and which was considered to be fluorenone ether, $(C_{13}H_9)_2O$. On the basis of the results which have been mentioned, it would be interesting to learn if this compound does not also follow a similar course of thermal decomposition.

Klinger and Standke [33] state that acetyl benzilic acid, $(C_6H_5)_2C<$ $OCOCH_3$ / CO_2H melts at 98°, and that at 100-110° it becomes transformed into benzilic acid very easily. It is not clear how it does so, however, and the fact is denied by Herzig and Schleiffer.

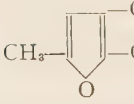
The behavior of another α-hydroxy acid, 2-thio-3-phenyl-4-hydroxy-1,2,3,4-tetrahydroquinazoline-4-carboxylic acid,  , has already been listed on p. 386.

[31] If small quantities are taken, benzilide may be distilled undecomposed.
[32] Friedlaender, *Ber.* **10**, 535 (1877).
[33] Klinger and Standke, *Ber.* **22**, 1212 (1889); Herzig and Schleiffer, *Ann.* **422**, 326 (1921).

Glyceric Acid. Glyceric acid is an α,β-dihydroxy acid, CH_2OH—$CHOH$—CO_2H. It has not been extensively studied, and its chief interest is its similarity in decomposition to tartaric acid. Debus [34] reported that a molecule of water was detached when the acid was kept at 105° for 10 hours. The viscid residue was capable of reverting to glyceric acid on treatment with bases.

Dry distillation [35] of glyceric acid yields water, carbon dioxide, pyruvic acid, and pyrotartaric acid, all of which are also formed from tartaric acid by heat. Formic and acetic acids may also be isolated in both of these cases.[36] It may be said in passing that glyceric acid is not a transient product in the pyrolysis of tartaric acid.[37] Instead, the reason for the similarity of the products in the two cases must rest in the fact that they are both α,β-dihydroxy acids.

Tartaric Acid. The names "pyrotartaric", "pyroracemic" and "pyrotritaric" acids for $HO_2C—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CO_2H$, $CH_3—CO—CO_2H$ and



, respectively, are suggestive of the fact that these compounds, among others, are formed when tartaric acid is heated. It has been established, however, that these compounds are not simple decomposition products, but instead are of secondary origin. It is interesting to note [38] that *meso*-tartaric acid is largely changed into racemic acid at 200°. About one-third of the acid is simultaneously decomposed into gaseous products.

Much of the early literature [39] dealing with the decomposition of tartaric acid at, or near, its melting point is obscured by such terms as tartralic, tartrelic, *iso*tartridic and ditartrylic acids. From the recent work of Chattaway and Ray,[40] it seems that these substances merely represent stages in the production of the acid lactide. This transition was found to be fairly complete at 150-165° (bath temperature), and 10-20 mm. pressure. Approximately one mol of water is lost, and action eventually ceases at this temperature. The lactide neutralizes about half the quantity of alkali that the original tartaric acid is capable of neutralizing. Additional base gradually hydrolyzes the inner ester (lactide):

[34] Debus, *Ann.* **106**, 83 (1858).
[35] Moldenhauer, *Ann.* **131**, 338 (1864).
[36] Böttinger, *Ber.* **10**, 268 (1877); *Ann.* **196**, 92 (1879).
[37] Böttinger, *Ann.* **188**, 314 (1877).
[38] Dessaignes *Ann.* **136**, 212 (1865).
[39] Fremy, *Ann. chim.* [2] **68**, 355 (1838); *Ann.* **78**, 301 (1851); Schiff, *Ann.* **125**, 132 (1863); Laurent and Gerhardt, *J. prakt. Chem.* **46**, 361 (1849).
[40] Chattaway and Ray, *J. Chem. Soc.* **119**, 34 (1921).

$$2HO_2C{-}CHOH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CO{-}OH \longrightarrow$$

$$HO_2C{-}CHOH{-}\underset{\displaystyle O}{\underset{|}{CH}}{-}CO{-}\underset{\displaystyle O}{\underset{|}{O}} + 2H_2O.$$

$$\underset{\displaystyle O}{\underset{|}{O}}{-}CO{-}\underset{\displaystyle O}{\underset{|}{CH}}{-}CHOH{-}CO_2H$$

The second stage in the pyrolysis of tartaric acid, according to Chattaway and Ray, occurs at about 180° (vacuum). Under these conditions carbon monoxide and carbon dioxide are gaseous products, and formic, acetic and pyruvic acids appear in the distillate. The fact that the residue is negligible, and that the quantitative estimation of the products of decomposition account for practically all of the original tartaric acid, make it evident that there can be no other primary products of decomposition. From 1 mol of tartaric acid (150 grams), 148.6 grams of decomposition products are formed as follows:

Water, 1 mol (18.8 grams); carbon dioxide, 1 mol (43 grams); carbon monoxide, 0.76 mol (21.3 grams); acetic acid, 0.82 mol (49 grams); pyruvic acid, 0.16 mol (14.1 grams); and formic acid, 0.052 mol (2.4 grams). There is a loss of 1.4 grams.

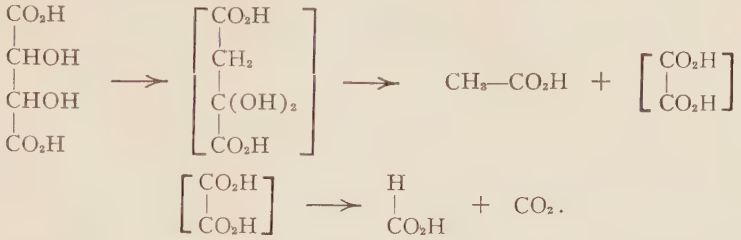
When tartaric acid, instead of the lactide, is heated directly at 180° (vacuum) the percentage of carbon dioxide in the evolved gas is considerably increased.

Since tartaric acid is not only an α-hydroxy acid, but also a β-hydroxyacid, or a glycol, or an α,β-dicarboxylic acid, any interpretation of these results must be highly speculative. One might anticipate that a "tartaric anhydride", similar to succinic anhydride might be produced by thermal means, but there is no evidence to support this. Also, one might anticipate that the lactide of tartaric acid would decompose in the manner of other lactides, in which case carbon monoxide would be evolved. Glycollic aldehyde and carbon dioxide should then be formed, due to the decomposition of an unstable β-aldehyde-acid:

$$[HO_2C{-}CHOH{-}CHO] \longrightarrow CO_2 + CH_2OH{-}CHO.$$

However, glycollic aldehyde has never been reported as a decomposition product of tartaric acid. Therefore, either the structure of the lactide is incorrect, or it decomposes in a peculiar manner. Chattaway and Ray have adopted the latter assumption, and postulated various rearrangements of the hydroxyl groups in the lactide. Their interpretation assumes that the lactide must rearrange first to the lactide of a hypothetical α,α-dihydroxysuccinic acid, which then immediately decomposes in two ways, giving acetic acid by one course, and pyruvic acid (after another rearrangement) by the other. Thus:

To account for the small amount of formic acid which was produced, these investigators assume a rearrangement of the original tartaric acid into α,α-dihydroxysuccinic acid, which breaks down to oxalic acid and eventually to formic acid:



Justification for this latter rearrangement is sought in the observation that sodium oxalate is one of the primary products when a tartrate is fused with sodium hydroxide. In such alkali fusions, however, there is a definite oxidizing action,[41] accompanied by the liberation of hydrogen. It is more logical to assume that the alkali decarboxylates the tartrate forming ethylene glycol, which then becomes immediately oxidized to the oxalate. This would provide no similarity to the proposed mechanism for the pyrolysis. Furthermore, oxalic acid has never been isolated from tartaric acid when the latter is heated alone.

Since tartaric acid is both an α- and a β-hydroxy acid, it would seem not unreasonable for it to undergo pyrolysis by a method common to both types, namely, dehydration to an unsaturated acid. In such an event, the following reaction would occur:

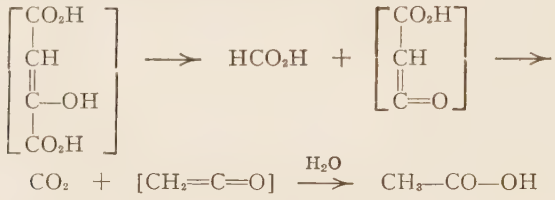
This unsaturated acid is the enol form of a β-ketonic acid, so that it should immediately decompose into carbon dioxide and pyruvic acid:

In support of this reaction mechanism, there is the observation of Chattaway and Ray that much more carbon dioxide is formed when the heating is not performed slowly, thereby avoiding the dehydration to the lactide. Further support is given by the fact that pyruvic acid is best prepared [42] from tartaric acid by heating in the presence of potassium bisulfate, a dehydrating agent (see p. 455, for mucic acid).

This mechanism not only explains the formation of pyruvic acid, but also permits an explanation of the presence of formic acid without neces-

[41] Fry and Schulze. *J. Am. Chem. Soc.* **48**, 958 (1926).
[42] *Organic Syntheses*, Vol. IV, New York, John Wiley and Sons, 1925, p. 64.

sitating a "hydroxyl wandering". The enol form, $HO_2\overset{1}{C}-\overset{2}{C}H=\overset{3}{C}(OH)-\overset{4}{C}O_2H$, is seen to contain two single bonds and one double bond in the carbon chain. Scission of one of the single bonds has already been mentioned in the formation of pyruvic acid which is undoubtedly the chief reaction. However, scission at the other single bond (between atoms 3 and 4) is not unreasonable, in which case formic acid and acetic acid would result, the latter through the medium of ketene. It could be predicted that scission would not occur at the double bond, because carbon atoms, quite generally, become severed much easier if connected by single bonds than by double bonds. It should be noticed that the prediction of a transitory ketene molecule is what one would expect from an α-hydroxy acid that possesses α,β-unsaturation.

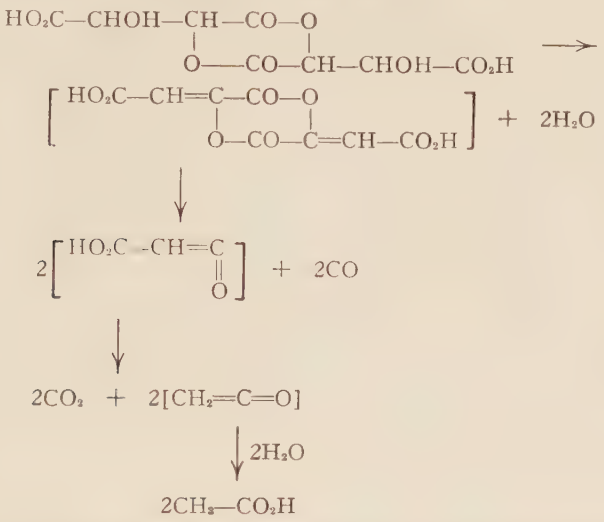


Of course, ketene could not be isolated in such surroundings.

Admittedly, all this is speculative, but at least the proposed mechanism explains the known facts rather well. However, reference to the data on p. 437 shows that formic and pyruvic acids are of relatively little importance as decomposition products of the lactide of tartaric acid. Acetic acid is the major product, and it is interesting to note that equimolecular quantities of carbon monoxide and acetic acid are produced from the lactide if 0.052 mol of the acetic acid is considered to be formed from the original tartaric acid instead of the lactide. The number 0.052 is the number of mols of formic acid from Chattaway and Ray's data (above), and according to the above mechanism, 0.052 mol of acetic acid should have formed simultaneously. Thus, from 1 mol of tartaric acid, through the lactide, there was formed 0.76 mol of carbon monoxide and 0.768 mol of acetic acid.

To obtain acetic acid from the lactide, Chattaway and Ray deemed it necessary to postulate a rearrangement prior to the decomposition (see p. 438). Although this interpretation may be correct, an alternative interpretation, which assumes no "hydroxyl wandering", is also conceivable. Prior to, or simultaneously with, the decomposition of the lactide, water may be eliminated to form an ethylenic bond. Rupture of the

lactone ring would then yield carbon monoxide and ketene (or ketene carboxylic acid), the ketene absorbing water to form acetic acid:



Part of the water may have been utilized in effecting the hydrolysis of a portion of the unchanged lactide to tartaric acid, which would then be free to undergo pyrolysis into pyruvic acid, or into formic acid, as outlined above.

Liebermann [43] found that when 100 parts of tartaric acid were mixed with 33 parts of glass powder, resinous and tarry products were formed on distillation. From this, 3.7 parts of pyruvic acid, 0.8 part of pyrotartaric acid, and 0.16 part of formic acid were identified. Another investigator [44] mixed tartaric acid with an equal quantity of pumice and obtained a 7 percent yield of pyrotartaric acid by distillation. In these experiments, acetic acid, carbon dioxide, and a trace of formic acid [45] were also observed.

Bechamp's directions [46] for the preparation of pyrotartaric acid advise melting the tartaric acid (400 grams) and heating for 15-20 minutes till acid vapors start to escape. The melt is then mixed with pumice (400 grams), cooled, pulverized, and distilled during 8-9 hours from a retort. About 20 percent yield of pyrotartaric acid (325 grams from 1600 grams of tartaric acid) may be realized. Bechamp reasoned that pyrotartaric anhydride came from an anhydride of tartaric acid, so that better yields should be expected if the anhydride were heated.

[43] Liebermann, *Ber.* **15**, 428 (1882).
[44] Arppe, *Ann.* **66**, 74 (1848).
[45] Völckel, *Ann.* **89**, 75 (1854).
[46] Bechamp, *Compt. rend.* **70**, 1000 (1870).

Berzelius [47] also noted the presence of pyruvic and acetic acids, as well as small amounts of pyrotartaric acid in the distillate from the dry-distillation of tartaric acid. Bourgoin [48] reported about a 1 percent yield of "dipyrotartracetone", $C_{16}H_{24}O_4$, in the same manner. Pyrotritaric acid, or 2,5-dimethylfuran-3-carboxylic acid, has also been mentioned as one of the products of pyrolysis. That it is formed in trivial yields is apparent from the fact [49] that only 1.2 grams of it results from the dry-distillation of 1 kg. of tartaric acid. Pyruvic acid undoubtedly plays an important part in these reactions. Its mode of pyrolysis into pyrotartaric acid has been mentioned on p. 355.

Other Dihydroxy Acids. Dihydroxy acids which are both α- and γ-hydroxy-acids always behave like γ-hydroxy-acids and form γ-lactones. Only one such case will be mentioned here. Others will be deferred till the systematic treatment of γ-hydroxy acids. α,α'-Dihydroxyadipic acid [50] is changed into the dilactone at 160-170° and 25 mm.:

$$(\text{—CH}_2\text{—CHOH—CO}_2\text{H})_2 \longrightarrow \text{O—CO—CH—CH}_2\text{—CH}_2\text{—CH—CO—O} + 2\text{H}_2\text{O}.$$

α,α'-Dihydroxysebacic acid behaves exclusively as an α-hydroxy acid, yielding at 230° [51] the dialdehyde related to suberic acid:

$$\text{HO}_2\text{C—CHOH—(CH}_2)_6\text{—CHOH—CO}_2\text{H} \longrightarrow \text{H—CO—(CH}_2)_6\text{—CHO} + 2\text{CO} + 2\text{H}_2\text{O}.$$

β-Hydroxy Acids.

Aliphatic β-Hydroxyacids. Quite characteristically, the β-hydroxyacids change into α,β-unsaturated acids by heating. In some cases this decomposition is completed by distillation, and in other cases not, particularly with the simpler acids. Hydracrylic acid, β-hydroxybutyric acid and β-hydroxyvaleric acid all [52] become partially dehydrated on distillation, according to the general equation:

$$\text{R—CHOH—CH}_2\text{—CO}_2\text{H} \longrightarrow \text{R—CH=CH—CO}_2\text{H} + \text{H}_2\text{O}.$$

The distillation temperature [53] for α-methyl-β-hydroxy-butyric acid is about 180°. It gives an oily distillate from which crystals of α-methylcrotonic acid gradually separate.

[47] Berzelius, *Ann. Physik* **36**, 5 (1835).
[48] Bourgoin, *Bull. soc. chim.* [2] **29**, 309 (1878).
[49] Wislicenus and Stadnicki, *Ann.* **146**, 306 (1868).
[50] LeSueur, *J. Chem. Soc.* **93**, 719 (1908).
[51] LeSueur, *ibid.* **91**, 1367 (1907).
[52] Moldenhauer, *Ann.* **131**, 335 (1864); Fittig and Spenzer, *Ann.* **283**, 79 (1894).
[53] Rohrbeck, *Ann.* **188**, 235 (1877).

β-Hydroxy-*iso*caproic acid [54] gives rise not only to the anticipated unsaturated acid, $(CH_3)_2CH—CH{=}CH—CO_2H$, but also to its isomer, pyroterebic acid, $(CH_3)_2C{=}CH—CH_2—CO_2H$. The latter compound may have been formed directly, or it may have resulted by rearrangement of the α,β-unsaturated acid. As would be expected, *iso*caprolactone, $(CH_3)_2C—CH_2—CH_2$ / $O———CO$, is also a product of this reaction (see pp. 368-9).

In the following two cases there is not only dehydration but also decarboxylation. The pyrolysis of α-ethyl-β-tolyl-β-hydroxy-propionic acid occurs [55] when it is kept at its melting point (134°), or when it is boiled in water:

$$CH_3C_6H_4—CHOH—CH(C_2H_5)—CO_2H \longrightarrow CH_3C_6H_4—CH{=}CH—C_2H_5 + H_2O + CO_2.$$

A part of α-methyl-β-hydroxy-*iso*heptylic acid,[56]

$$(CH_3)_2CHCH_2—CHOH—\underset{\displaystyle CH_3}{\underset{|}{C}}H—CO_2H$$

distils without decomposition, the remainder pyrolyzing into water, carbon dioxide and an olefine.

That the dehydration reaction is not the only one to be considered for β-hydroxy acids is evident from a study of the α,α-dialkyl homologs. The scission which occurs in such cases has already been mentioned (p. 166). α,α-Diethyl-β-hydroxybutyric acid, at 190°, becomes transformed [57] into acetaldehyde and α-ethyl-butyric acid, and similarly, α-methyl-α-propyl-β-hydroxy-butyric acid decomposes [58] into acetaldehyde at 170°; the general equation for both is:

$$CH_3—\underset{\displaystyle OH}{\underset{|}{C}}H—CR_2—CO_2H \longrightarrow CH_3—CHO + H—CR_2—CO_2H.$$

In the latter case, all the volatile material distils at 200°, leaving a small residue, non-volatile at 260°, which may have been an "ester-anhydride".

These two cases are interesting inasmuch as no hydrogen atom exists on the α-carbon atom. The only chance for a molecule of water to be eliminated, therefore, would be for the hydroxyl to combine with a γ-hydrogen. Since, in these cases, this has not occurred, it might be argued that pyroterebic acid could not have been a primary product

[54] Braun, *Monatsh.* **17**, 210 (1896).
[55] Matsurevitsh, *J. Russ. Phys. Chem. Soc.* **39**, 183 (1907); *Chem. Abstracts* **1**, 2113 (1907).
[56] von Reichstein, *J. Russ. Phys. Chem. Soc.* **39**, 310 (1907); *Chem. Abstracts* **1**, 2113 (1907).
[57] Schnapp, *Ann.* **201**, 62 (1880).
[58] Jones, *Ann.* **226**, 287 (1884).

from β-hydroxy-*iso*caproic acid (above). This alone, however, is insufficient evidence, for the γ-hydrogen in *iso*caproic acid is attached to a tertiary carbon instead of a primary.

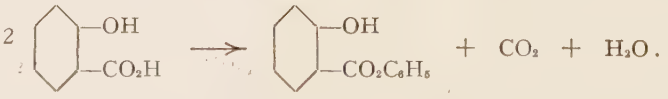
Salicylic Acid. This may be regarded as a β-hydroxy acid, but its course of pyrolysis must obviously differ from that of aliphatic β-hydroxy acids. It has long been recognized [59] that phenol is one of the products of distillation, particularly if it is done rapidly, but it has been definitely shown that the reaction is not one of simple decarboxylation. Even when heated in a test-tube, salicylic acid does not change smoothly into phenol. The first change—which occurs at temperatures above 200°—is one of esterification, with phenyl salicylate (salol) the resultant product. Phenyl salicylate, itself, starts to pyrolyze at temperatures above 280° into phenol, and if it is boiled gently till all the phenol is expelled,[60] a good yield of xanthone (61-63 percent) may be obtained.[61] This will be discussed in more detail under esters (pp. 540-5).

Kunz-Krause and Manicke [62] found the following percentages of carbon dioxide, when samples of salicylic acid were heated for 30-minute periods:

TABLE XLII. *Effect of Heat on Formation of Carbon Dioxide from Salicylic Acid.*

Temperature °C.	Carbon Dioxide Percent	
250°	7.40	
280°	9.94	
300°	10.70	
320°	11.38	(7.35 percent in 5 minutes)
340°	14.11	
350°	16.73	

The calculated amount of carbon dioxide for the following equation is 15.94 percent:



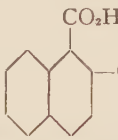
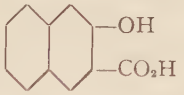
Because of the fact that small quantities of phenol were observed at 340-350° (and none below 280°), Kunz-Krause and Manicke favor Seifert's equation [63] to express the preliminary decomposition of phenyl salicylate:

[59] Klepl, *J. prakt. Chem.* [2] **28**, 217 (1883).
[60] Graebe, *Ber.* **21**, 501 (1888); *Ann.* **254**, 280 (1889).
[61] Holleman, *Organic Syntheses*, Vol. VII, New York, John Wiley and Sons, **1927**, p. 84.
[62] Kunz-Krause and Manicke, *Ber.* **53**, 190 (1920).
[63] Seifert, *J. prakt. Chem.* [2] **31**, 472 (1885).

An alternative equation by Graebe:

$$HO—C_6H_4—CO—OC_6H_5 + H_2O \longrightarrow 2C_6H_5OH + CO_2,$$

would require much more phenol than was observed experimentally. The formation of xanthone, $C_6H_4{<}\overset{O}{\underset{CO}{}}{>}C_6H_4$, from salol (or from disalicylide) is, of course, accompanied by the liberation of carbon dioxide (see esters).

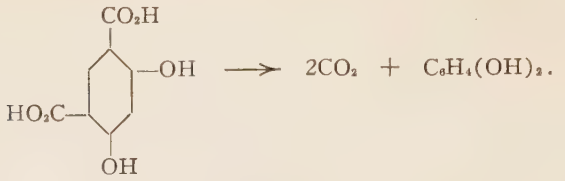
2-Hydroxy-1-naphthoic acid,[64]  , appears to be related to salicylic acid, but it is much less stable. With quick heating it melts at 156°, but if kept for a time at 124-128°, pyrolysis into carbon dioxide and β-naphthol sets in. Lesser [65] mentions a rearrangement of this compound to  at 250°. However, the phenyl esters of these compounds resemble salol and yield xanthones.

Kostanecki [66] employed a useful device in going from the hydroxynaphthoic acids to the xanthones by distilling the acids in the presence of acetic anhydride, a method [67] which Perkin had successfully introduced with salicylic acid. Since aspirin is thermally decomposed to xanthone, (see p. 545) there is every reason to believe that the acetate ester is formed and then pyrolyzed in this process.

Possibly a mechanism similar to the above could be adopted to explain the decarboxylation [68] of methylene disalicylic acid, $CH_2\left(C_6H_3{<}\overset{OH}{\underset{CO_2H}{}}\right)_2$, but as yet, no ester (corresponding to salol from salicylic acid) has been reported. When kept above its melting point for a short time, it yields a mixture of hydroxyphenyl-methylene salicylic acid and methylene diphenol.

At its melting point, 192°, resorcinol dicarboxylic acid yields [69] carbon dioxide and resorcinol:

[64] Schmitt and Burkhard, *Ber.* **20**, 2701 (1887).
[65] Lesser, Kranepuhl and Gad, *Ber.* **58**, 2112 (1925).
[66] Kostanecki, *Ber.* **25**, 1640 (1892).
[67] Perkin, *Ber.* **16**, 338 (1883).
[68] Clemmensen and Heitman, *J. Am. Chem. Soc.* **33**, 739 (1911).
[69] Tiemann and Lewy, *Ber.* **10**, 2212 (1877).



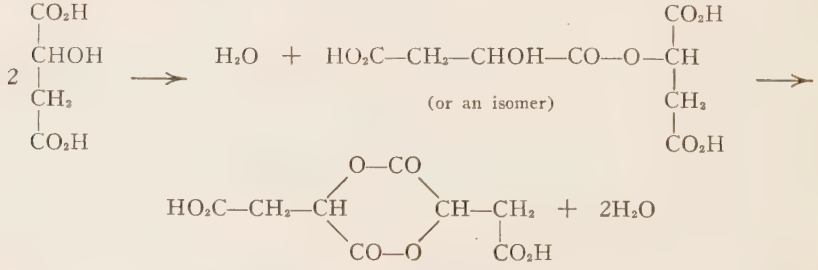
For other cases, see p. 344.

In connection with the esterification of salicylic acid to salol by thermal means, it is interesting to recall (p. 346) that the methoxybenzoic acids also behaved peculiarly when heated, *o*-methoxybenzoic acid for example, changing to a mixture of methyl salicylate and methyl *o*-methoxybenzoate.

β-Hydroxy Derivatives of Dicarboxylic Acids. The decomposition of hydroxymethyl-malonic acid into acrylic acid follows from the fact that it is a β-hydroxy acid, but also that it is a compound related to malonic acid. Hydroxymethyl malonic acid [70] is a syrupy liquid which decomposes above 113°:

$$HO{-}CH_2{-}CH(CO_2H)_2 \longrightarrow H_2O + CO_2 + CH_2{=}CH{-}CO_2H.$$

Malic acid may be regarded as an α- or a β-hydroxy acid. It is also related to succinic acid. As an α-hydroxy acid, it should form an ester-like anhydride; as a β-hydroxy acid (also true of some α- acids) it should form an unsaturated acid; and as a derivative of succinic acid, it should form an acid anhydride. These three types of decomposition are encountered, successively, between 100-200°. In the air at 100°, or in a vacuum of 25 mm. at 160°, malic acid changes [71] into the ester, malomalic acid. Continued heating (at 180° and 40-60 mm. for 3 hours) results in the formation of malide. These changes are probably represented as follows:



Malide is also one of the products when malic acid is heated for a short time at 210°, but the major tendency of this reaction is the formation

[70] Coops, *Rec. trav. chim.* **23**, 355 (1904); **20**, 430 (1901).
[71] Walden, *Ber.* **32**, 2707 (1899).

of maleic anhydride. At 140-150°, fumaric acid [72] begins to predominate in the products of pyrolysis, and maleic anhydride predominates at 180-200°:

$$\begin{matrix} HO{-}CH{-}CO_2H \\ | \\ HCH{-}CO_2H \end{matrix} \longrightarrow \begin{matrix} CH{-}CO \\ \| \\ CH{-}CO \end{matrix} >O + 2H_2O.$$

Similarly, dimethyl maleic anhydride [73] results when dimethyl malic acid, $\begin{matrix} CH_3{-}CH{-}CO_2H \\ | \\ CH_3{-}C(OH){-}CO_2H \end{matrix}$, is heated.

A means of analyzing for malic acid [74] in the presence of tartaric or citric acids has been developed from the standpoint of pyrolysis. If 0.05 gram of *malic acid* in a test tube is heated by a direct flame, there is formed a copious white sublimate of fumaric acid, whose ammonium salt reacts with the silver ion to yield a precipitate of silver fumarate. Neither of the other two hydroxy acids behave similarly. As has been shown, one of the products from *tartaric acid* is pyruvic acid. This may be formed and identified by a similar test-tube method of pyrolysis. After the heating, the mass is dissolved in water and then made alkaline with sodium hydroxide. Indigotin is formed from this by addition of *o*-nitrobenzaldehyde, and chloroform reveals it as an intense blue layer. If *citric acid* is treated in the manner of malic acid, the silver salt which is produced (from the ammonium salt, as before) is not silver fumarate. It dissolves in boiling water, and reappears on cooling. Citric acid will be discussed in detail shortly.

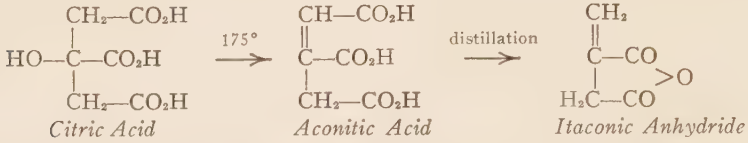
Vacuum distillation [75] of β-hydroxyglutaric acid leads to a mixture of glutaconic acid, vinylacetic acid [76] and also glutaconic anhydride.[77] It will be recalled that compounds with the glutaconic acid skeleton become decarboxylated by heat (p. 415), so that vinylacetic acid in this case undoubtedly comes from glutaconic acid.

$$HO_2C{-}CH_2{-}CHOH{-}CH_2{-}CO_2H \begin{matrix} \nearrow HO_2C{-}CH{=}CH{-}CH_2{-}CO_2H + H_2O \\ \searrow CH_2{=}CH{-}CH_2{-}COH_2 + H_2O + CO_2 \end{matrix}$$

Citric Acid. Citric acid differs in structure from β-hydroxyglutaric acid by the presence of an additional carboxyl group. The modes of pyrolysis of these two acids are surprisingly similar. Aconitic acid, which corresponds to glutaconic acid, and itaconic acid, which

[72] Skraup, *Monatsh.* **12**, 117 (1891); Pictet, *Ber.* **14**, 2648 (1881); van't Hoff, *Rec. trav. chim.* **4**, 419 (1885); Walden, *Ber.* **32**, 2706 (1899); Aberson, *Ber.* **31**, 1440 (1898).
[73] Michael and Tissot, *J. prakt. Chem.* [2] **46**, 300 (1892).
[74] Sanchez, *Anales asoc. quim. Argentina*, **24**, 356 (1926).
[75] von Pechmann and Jenisch, *Ber.* **24**, 3250 (1891).
[76] Fichter and Krafft, *Chem. Zentr.* **1898**, II, 1011; *Ber.* **32**, 2799 (1899); Autenrieth, *Ber.* **38**, 2547 (1905).
[77] Perkin and Tattersall, *J. Chem. Soc.* **87**, 365 (1905).

corresponds to vinylacetic acid, are the initial products [78] that are formed when citric acid is heated. The former is produced at 175°, and the latter at distillation temperature: [79]

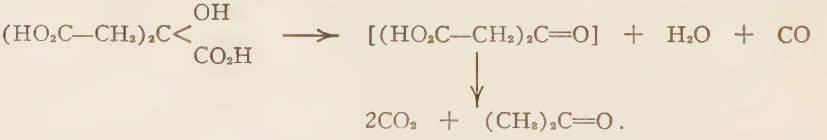


Citric Acid *Aconitic Acid* *Itaconic Anhydride*

Since itaconic acid is so intimately related in structure to succinic acid, itaconic anhydride, and not itaconic acid, is produced. However, the major product of the distillation is not itaconic anhydride, but its isomer citraconic anhydride. The relationship of these two substances has already received comment (p. 407). If itaconic anhydride [80] is distilled nearly pure citraconic anhydride results.

Goebel [81] reported a yield of 175 grams of pure citraconic anhydride from 1 kg. of anhydrous citric acid.

Acetone is also a product [82] of this thermal decomposition. Since citric acid is an α-hydroxy acid as well as a β-hydroxy acid, this is very reasonable. Just as α-hydroxy acids have been shown to eliminate carbon monoxide with the production of a carbonyl group, so citric acid should form acetone from a transient acetone dicarboxylic acid (a β-ketonic acid):



β-Lactones. It is appropriate to mention β-lactones at this point to emphasize the fact that they have never been prepared by the pyrolysis of β-hydroxy acids, nor is there evidence to lead one to believe that such a tendency exists. Even with α,α-dialkyl-β-hydroxy acids, this is true. It will be recalled that these compounds decompose into an aldehyde and an acid:

[78] Crasso, *Ann.* **34**, 56 (1840); Pawolleck, *Ann.* **178**, 153 (1875); Swarts, *Jahresbericht*, 1873, 579.
[79] Swarts, *loc. cit.*; Gottlieb, *Ann.* **77**, 265 (1851).
[80] Lassaigne, *Ann. chim.* [2] **21**, 100 (1822); Crasso, *loc. cit.*
[81] Goebel, *J. Am. Chem. Soc.* **47**, 1990 (1925).
[82] von Pechmann, *Ber.* **17**, 2543 (1884).

β-Lactones decompose in an entirely different manner [83] from β-hydroxy acids, since carbon dioxide is quite generally eliminated and this is accompanied by the formation of an unsaturated compound. For example: [84]

$$\left[\begin{array}{l} R_2C{-}CO \\ \quad | \quad | \\ R_2C{-}O \end{array}\right] \longrightarrow R_2C{=}CR_2 + CO_2.$$

Salkowski [85] prepared β-butyrolactone and observed that it pyrolyzes into propylene and carbon dioxide. Similarly, the α-ethyl homolog gives pentene-2, and α,α-dimethyl-β-butyrolactone gives trimethyl ethylene:

$$\begin{array}{l} CH_3{-}CH{-}C(CH_3)_2 \\ \quad\quad | \quad\quad | \\ \quad\quad O{-}{-}CO \end{array} \longrightarrow CH_3{-}CH{=}C(CH_3)_2 + CO_2.$$

In a discussion of β-lactones, Johansson and Hagman [86] conclude that their formation is no more unusual than the formation of γ-lactones (from the β- or the γ-bromo acids). They point out, however, that the formation of β-hydroxy acids is irreversible, and should be avoided.

Carbon dioxide is a product of the thermal decomposition of $\begin{array}{l}(C_6H_5)_2C{=}C{-}CH{-}O{-}COCH_3 \\ \quad\quad\quad\quad | \quad | \\ \quad\quad\quad\quad O{-}CO \end{array}$, but no other products [87] could be identified. Compounds related to allene or to ketene were anticipated. Kohler [88] describes a stable compound of this type, γ-benzoyl-β-phenyl-β-butyrolactone, $\begin{array}{l} C_6H_5CO{-}CH_2{-}C(C_6H_5){-}CH_2 \\ \quad\quad\quad\quad\quad\quad | \quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad O{-}{-}{-}{-}{-}{-}{-}CO \end{array}$, which is not decomposed at 200°. Above that temperature, carbon dioxide is not evolved, but a complex pyrolysis sets in. See p. 371.

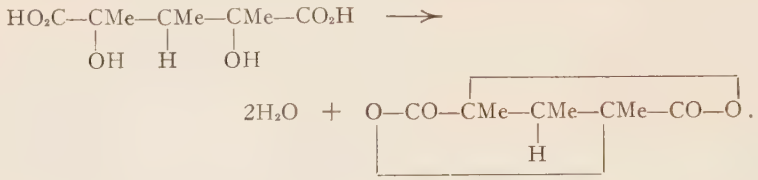
γ-Hydroxy Acids.

The aliphatic γ-hydroxy acids exhibit such a tendency to change into γ-lactones that they are practically non-existent, except in water solutions. Some of these compounds such as γ-hydroxybutyric acid and its α-ethyl homolog have been found [89] to be stable at very low temperatures. The general equation is:

$$\begin{array}{l} R{-}CH{-}CH_2{-}CH_2 \\ \quad\quad | \quad\quad\quad | \\ \quad OH \quad HO_2C \end{array} \longrightarrow \begin{array}{l} R{-}CH{-}CH_2{-}CH_2 \\ \quad\quad | \quad\quad\quad | \\ \quad\quad O{-}{-}{-}{-}{-}{-}{-}CO \end{array} + H_2O.$$

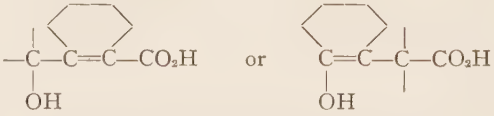
[83] For β-lactonic acids, see p. 365.
[84] Staudinger, *Ann.* **356**, 63 (1907); Staudinger and Kon, *Ann.* **384**, 38 (1911).
[85] Salkowski, *J. prakt. Chem.* **106**, 253 (1923).
[86] Johansson and Hagman, *Ber.* **55**, 647 (1922).
[87] Staudinger and Reber, *Helv. Chim. Acta* **4**, 9 (1921).
[88] Kohler, *Am. Chem. J.*, **46**, 476 (1911).
[89] Fittig and Chanlarow, *Ann.* **226**, 325, 384 (1884).

Hydroxy acids in the glutaric series form lactones, apparently in preference to acid anhydrides. Distillation of trimethyl dihydroxy glutaric acid [90] at ordinary pressure yields the dilactone:



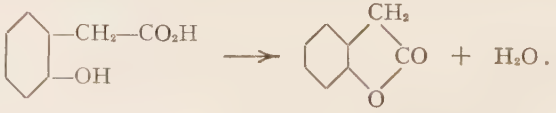
d-Erythronic acid, $HO_2C—(CHOH)_4—CO_2H$, is a sirup which becomes [91] lactonized during the evaporation of its aqueous solution. The *d,l*-acid behaves similarly by evaporating [92] its concentrated aqueous solution at 100° and 15 mm. For other hydroxy acids of the sugar group, see under δ-hydroxy acids.

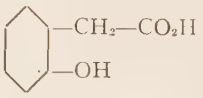
When part of the functional group for γ-hydroxy acids exists in an aromatic nucleus, γ-lactones may still be formed, either spontaneously or by heating, provided that the carboxyl or the hydroxyl is on a side chain. In other words, the permissible structures for lactonization must possess either of the following two skeletons:



No more than two nuclear carbon atoms (*ortho* atoms) may be present. Thus, *m*-hydroxybenzoic acid exhibits no tendency to form a lactone, although the hydroxyl and carboxyl are separated by three carbon atoms. The following cases illustrate lactone formation.

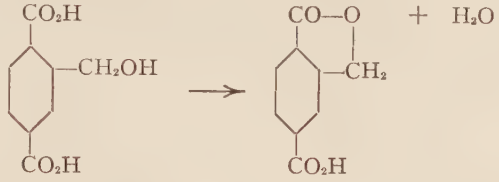
o-Hydroxyphenylacetic acid is isolable,[93] and passes into a lactone by distillation with a free flame:



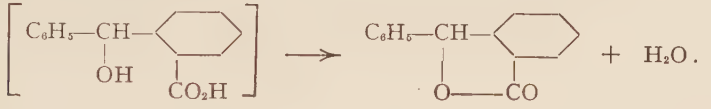
2,5-Dihydroxyphenylacetic acid,  , is lactonized [94] above 100°.

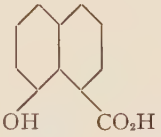
[90] Zelinsky and Tschugajew, *Ber.* **28**, 2941 (1895).
[91] Ruff, *Ber.* **32**, 3678 (1899).
[92] Nef, *Ann.* **357**, 248 (1907).
[93] Baeyer and Fritsch, *Ber.* **17**, 975 (1884).
[94] Wolkow and Baumann, *Z. physiol. Chem.* **15**, 253 (1891).

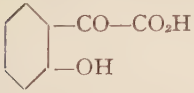
Hydroxymethyl-terephthalic acid,[95] if maintained for an hour at 100°, is dehydrated to 4-carboxy-1,2-phthalide:



Benzohydrol-*o*-carboxylic acid [96] is not known, but only exists in the form of phenylphthalide:



At its melting point, 169°, 8-hydroxy-1-naphthoic acid,  , changes [97] into the lactone.

Protocatechuic acid and gallic acid, which have already been discussed (p. 343), illustrate the behavior of *m*-hydroxy acids. The essential reaction in both cases is one of decarboxylation into catechol and pyrogallol, respectively, although side reactions leading to hydroxyanthraquinones are also encountered. *o*-Hydroxyphenylglyoxylic acid,[98]  , may be regarded, to be sure, as a γ-hydroxy acid, but essentially it is an α-keto acid. It is reported to yield salicylic acid on distillation (p. 356). For γ- and δ-lactonic acids, see an earlier chapter (pp. 367, 371).

δ-Hydroxy Acids.

Delta-hydroxy acids are remarkably like the *gamma*-hydroxy acids in their thermal behavior. The simple members of both systems are difficult to isolate because of the ease of lactone formation. δ-Hydroxy-*n*-valeric acid may be isolated [99] as an oil. It appears to distil between 110-120° at 13-14 mm., but a polymer of δ-valerolactone comprises most of the distillate.

[95] Perkin and Stone, *J. Chem. Soc.* **127**, 2275 (1925).
[96] Rotering, *Jahresbericht der Chemie* **1875**, 596; Gresly, *Ann.* **234**, 235 (1886).
[97] Ekstrand, *Ber.* **19**, 1138 (1886).
[98] Schad, *Ber.* **26**, 221 (1893).
[99] Fichter and Beisswenger, *Ber.* **36**, 1201 (1903).

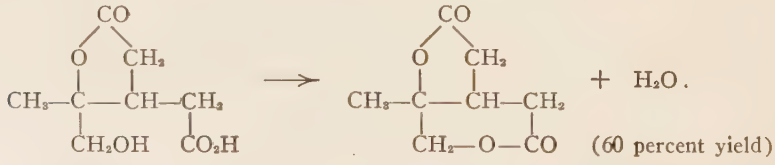
This same property of lactonization is apparent in the formation of dilactones from certain dihydroxy dicarboxylic acids. Thus, the racemic form of α,α'-dihydroxyadipic acid would certainly be renamed δ,δ'-dihydroxyadipic acid, were pyrolysis the basis for nomenclature. At 160-170° and 25-30 mm. it becomes dehydrated [100] to the dilactone:

$$(-CH_2-CHOH-CO_2H)_2 \longrightarrow 2H_2O + O{-}CO{-}CH{-}CH_2{-}CH_2{-}CH{-}CO{-}O.$$

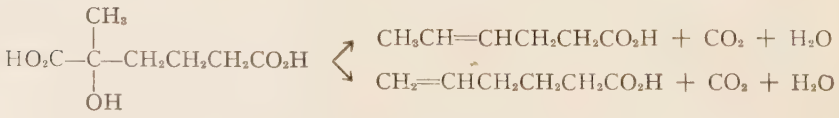
The *meso* form of this acid gives a modification of this reaction. The compound formed at 180-190° and 35-40 mm. possesses the empirical formula $C_{12}H_{14}O_9$. Possibly its structure is

$$HO_2C{-}CH{-}CH_2{-}CH_2{-}CH{-}O{-}CO{-}CH{-}CH_2{-}CH_2{-}CHOH.$$

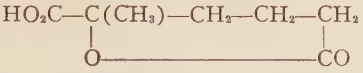
Either the high-melting or the low-melting forms of α,α'-dihydroxy-α,α'-dimethyladipic acid change by heating [101] under reduced pressure into a mixture of the lactonic acid, $HO_2C{-}CMe{-}CH_2{-}CH_2{-}CMe{-}OH$ (O—CO), and the dilactone, $O{-}CO{-}CMe{-}CH_2{-}CH_2{-}CMe{-}CO{-}O$. Similarly, distillation of α,α'-dihydroxy-α-methyl-α'-*iso*propyl-adipic acid [102] yields its dilactone; and hydroxy-terpenylic acid, a lactonic acid, is changed [103] into a dilactone by vacuum distillation:

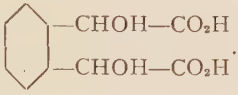
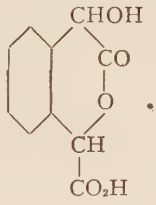


A mixture of γ-ethylidene butyric acid and β-allylpropionic acid results when α-methyl-α-hydroxyadipic acid is distilled. This distillation [104] commences at about 300°.



[100] LeSueur, *J. Chem. Soc.* **93**, 724 (1908).
[101] Fittig, *Ann.* **353**, 57 (1907).
[102] Wallach, *Ann.* **356**, 212 (1907); **362**, 267 (1908).
[103] Best, *Ber.* **27**, 1222, 3333 (1894).
[104] Fichter and Langguth, *Ber.* **30**, 2050 (1897); *Ann.* **313**, 375 (1900).

Here there is competition between an α- and a δ-hydroxy acid, with little doubt that the tendency of the latter for lactonization should be dominant. In such an event, the unsaturated acids which were isolated would be pyrolytic products of the lactonic acid, 
(see p. 371). However, the behavior of δ-lactonic acids, with a δ-carboxyl group, has been insufficiently studied to provide a trustworthy analogy.

Another acid which is both an α- and a δ-hydroxy acid is α,α'-dihydroxy-*o*-phenylenediacetic acid,  . If heated [105] at 110°, this loses a molecule of water, giving the lactonic acid,  . This lactonic acid is of the type referred to above, but its behavior on further heating seems not to have been investigated.

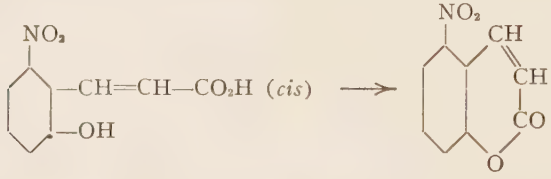
As with the γ-hydroxy acids, the two *ortho* carbon atoms of an aromatic nucleus may participate in the skeleton of δ-hydroxy acids without destroying the ability to form the lactone. When three or four nuclear carbon atoms participate, as in the case of *p*-hydroxybenzoic acid, this behavior is never observed. Instead, *p*-hydroxybenzoic acid gradually changes into phenol and carbon dioxide [106] above its melting point, 210°. By distillation, about half of the decomposition appears to proceed in this way, but simultaneously a large amount of *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid, $HO—C_6H_4—CO—O—C_6H_4—CO_2H$, and lesser amounts of di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid [107] and "*para*oxybenzid", $(C_7H_4O_2)_x$, are formed as water is eliminated.

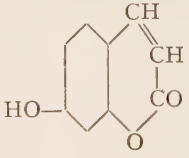
Hydroxy-β-phenylpropionic acid, better known as melilotic acid,[108] is readily changed into its lactone by distillation. From this, it might be argued that *o*-hydroxycinnamic acid (coumaric acid) should change into coumarin. This is not the case, however, and from this fact it may

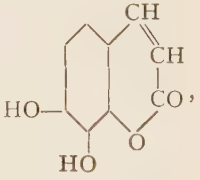
[105] Challenor and Ingold, *J. Chem. Soc.* **123**, 2066 (1923).
[106] Klepl, *J. prakt. Chem.* [2] **28**, 193 (1883).
[107] *See also* Fischer and Freudenberg, *Ann.* **372**, 32 (1910).
[108] Fittig and Hochstetter, *Ann.* **226**, 357 (1884).

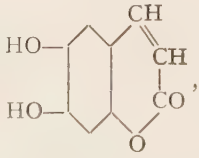
be argued that coumaric acid is the *trans*-acid, $HO{-}C_6H_4{-}\underset{\displaystyle H{-}C{-}CO_2H}{\overset{\displaystyle \|}{C}}{-}H$. Carbon dioxide is eliminated [109] instead at 200°. Cinnamic acid and caffeic acid (p. 349), with related structures, but with no *ortho*-hydroxyl group, behave in this manner. The *cis*-isomer, coumarinic acid, displays such a tendency for lactonization that it is known only in the form of its derivatives. For example, coumarin, and not coumarinic acid, results as carbon dioxide is passed into a solution of barium coumarinate. This suggests the great instability of coumarinic acid, and the ease by which it is transformed into coumarin.

o-Nitrocoumarinic acid is somewhat more stable.[110] In aqueous or in alcoholic solution, it is readily converted into *o*-nitrocoumarin by gentle boiling:



o-Nitrocoumaric acid, the *trans* isomer, is unchanged under these conditions. The ethyl ethers of coumaric and of coumarinic acid, $C_2H_5O{-}C_6H_4{-}CH{=}CH{-}CO_2H$, are isolable. Heating [111] of the latter (*cis*) produces a partial change into the former (*trans*), but there is some decomposition as well. Other similar compounds, which are related to *o*-hydroxycinnamic acid, are known best in the form of their lactones. In passing, umbelliferron, 

, and its methyl ether, herniarin, may be mentioned; also, daphnetin, 

, and aesculetin, 

, or its monomethyl ether, scopoletin.

[109] Zwenger, *Ann. Supplement* **8**, 24 (1872).
[110] von Miller and Kinkelin, *Ber.* **22**, 1705 (1889).
[111] Perkin, *Chem. News* **43**, 287 (1881); *J. Chem. Soc.* **39**, 409 (1881).

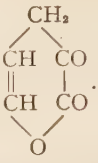
The lactones of *hydroxy acids in the sugar group* are all formed readily,[112] but not with equal ease in all cases. This difference is particularly well illustrated with mannonic and gluconic acids, both $HO—CH_2—(CHOH)_4—CO_2H$. Even in water solutions at 0°, the former gives the lactone rather quickly; at 100° the change is very rapid. Gluconic acid also lactonizes somewhat in cold solutions, but this process is incomplete even after several hours[113] at 100°.

Partial lactonization by evaporation of the aqueous solutions occurs in the case of *l*-ribonic acid.[114] *d*-Arabonic acid,[115] also $HOCH_2—(CHOH)_3—CO_2H$, is a sirup which changes into its lactone by heating on the water bath. Whether or not these and other similar lactones are of the γ- or δ- type is difficult to answer, although in the past the *gamma* form has been given the preference.[116]

Evaporation of the aqueous solution is sufficient to cause a partial lactonization[117] of *d,l*-galactonic acid, $CH_2OH—(CHOH)_4—CO_2H$. The same is true of *d*-gulonic acid[118] and of α-rhamnohexonic acid,[119] $CH_3—(CHOH)_5—CO_2H$, and of mucic acid,[120] $HO_2C—(CHOH)_4—CO_2H$. With mucic acid the empirical formula of the lactone (a sirup) is $C_6H_8O_7$. Saccharic acid[121] forms a crystalline lactone, melting point 130-132°.

Dry-distillation of mucic acid leads to quite different results. Possibly the lactone is the first stage in the pyrolysis, although this has not been established. Scheele first noticed a sublimate in the distillation of mucic acid. Trommsdorf[122] checked this result, as did Houton-Labillardière, who identified "pyromucic acid" and named it as such. From 150 grams of mucic acid (dry-distillation gave large amounts of carbon dioxide) a light residue of carbon, and 60 grams of a brown-colored liquid from which 8-10 grams of pure furoic acid, melting point 130°, was isolated. Acetic acid was also noted. Other recorded products from such a thermal decomposition[123] are carbon monoxide, water, formic

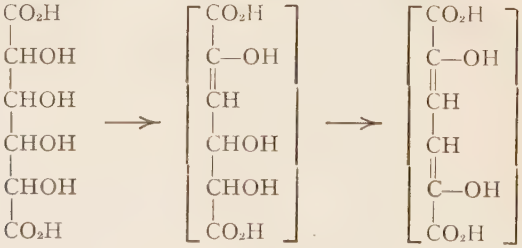
[112] Fischer, *Ber.* **27**, 3226 (1894).
[113] Kiliani and Kleeman, *Ber.* **17**, 1298 (1884); Fischer, *Ber.* **23**, 2613 (1890).
[114] Fischer and Piloty, *Ber.* **24**, 4216 (1891).
[115] Ruff, *Ber.* **32**, 556 (1899).
[116] For a discussion of the conflicting views in regard to the ring structures of hexoses, *see* "A Survey of American Chemistry," New York, The Chemical Catalog Co. **1925-1926**, **1**, p. 191.
[117] Fischer and Hertz, *Ber.* **25**, 1249 (1892).
[118] Fischer and Fay, *Ber.* **28**, 1981 (1895).
[119] Fischer and Tafel, *Ber.* **21**, 1658 (1888); Fischer and Piloty, *Ber.* **23**, 3104 (1890).
[120] Fischer, *Ber.* **24**, 2141 (1891).
[121] Sohst and Tollens, *Ann.* **245**, 6 (1888).
[122] Trommsdorf, *Ann. chim.* **71**, 79 (1809); Houton-Labillardière, *ibid.* [2] **9**, 365 (1818).
[123] Limpricht and Rohde, *Ann*, **165**, 256, 279 (1873).

acid, and small yields of *iso*pyromucic acid,  . The yield of the latter may be increased to 10 percent by distilling the mucic acid with potassium bisulfate.[124] This is suggestive of the change from tartaric acid to pyruvic acid, particularly in the presence of potassium bisulfate (p. 439). In Limpricht and Rohde's experiments, mucic acid (30 grams) was gently heated for 4 hours (in a retort which was but one-sixth full) so that one drop of distillate was collected every 2 minutes; in the remaining 4 hours (8 hours total), the retort was gradually heated to a dull red glow.

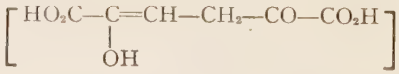
Klinkhardt and later Zenoni identified small amounts [125] of dehydromucic acid from a similar reaction mixture. Klinkhardt used a metal bath at 280°.

The steps in the dry-distillation of mucic acid are rather obscure. One has the option of assuming three different initial modes of dehydration: (1) as an α-hydroxy acid, giving a lactide; (2) as a β-hydroxy acid, giving an unsaturated acid; (3) as a γ- or δ-hydroxy acid, giving a γ- or δ-lactone. It is rather difficult, without numerous assumptions, to explain the formation of furoic, *iso*pyromucic, or dehydromucic acids by (1) or (3), but (2) fits the facts rather well.

As a β,β'-dihydroxy acid, mucic acid could lose one or two molecules of water. Note that it must be a β-hydroxyl which unites with an α-hydrogen.

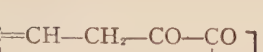
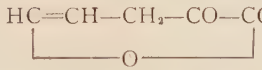
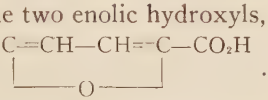


The di-enol, by rearrangement into its mono-keto isomer,

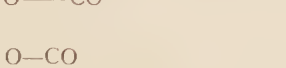


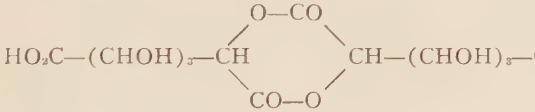
becomes an α-keto-δ-hydroxy acid. Ring closure to the δ-lactone,

[124] Simon, *Compt. rend.* **130**, 255 (1900).
[125] Klinkhardt, *J. prakt. Chem.* [2] **25**, 42 (1882); Zenoni, *Gazz. chim. ital.* **20**, 517 (1890); *see also* Oliveri and Peratoner *ibid* **19**, 632 (1889).

 , followed by decarboxylation, would then lead to *iso*pyromucic acid,  . Should the original di-enol produce a ring closure between the two enolic hydroxyls, dehydromucic acid would be formed:  .

Elimination of one of the two carboxyls by heat would give furoic acid, and loss of both would give furan. Furan has not been mentioned as a product of the decomposition of mucic acid, but it is undoubtedly formed (p. 363) and it may be cited as one of the reasons [126] for the poor yield of furoic acid.

It cannot be stated whether or not mucic acid (or similar sugar acids) form "lactides" in the manner of tartaric acid. The literature states that lactones are the initial product of dehydration. However, the reported values of *percent carbon, percent hydrogen* and the *titration* for the lactone,  , would be the same as for the lactide,



The molecular weight would differ but this seems never to have been determined. Until the lactide has been identified as a known product of the reaction, there is little use in trying to predict how it would pyrolyze. However, its decomposition might be expected to resemble that of the lactide of tartaric acid.

A striking type of ring closure [127] is that of *N*-hydroxyethyl sarkosine into 4-methyl-2-keto-morpholine by heating:

Hydroxyethyl sarkosine was synthesized from sarkosine and ethylene oxide. Strictly speaking, this is not a δ-hydroxy acid, since nitrogen is in the chain, but the ring closure resembles that of δ-lactones.

The chief reactions when cholic acid,[128] desoxycholic acid,[129] or

[125] *See*, for example, Sohst and Tollens, *Ann.* **245**, 21 (1888).
[127] Knorr, *Ann*, **307**, 199 (1899).
[128] Wieland and Weil, *Z. physiol. Chem.* **80**, 296 (1912).
[129] Wieland and Sorge, *ibid.* **98**, 63 (1916).

lithocholic acid [130] are distilled in a vacuum of 12 mm. are dehydration reactions to cholatrienic, choladienic and cholenic acids, respectively. The yields are good:

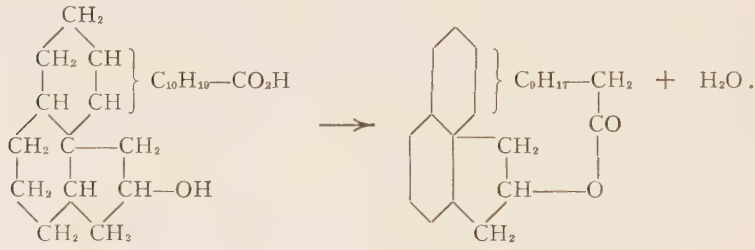
Cholic; $C_{23}H_{36}(OH)_3—CO_2H \longrightarrow C_{23}H_{33}—CO_2H + 3H_2O$

Desoxycholic; $C_{23}H_{37}(OH)_2—CO_2H \longrightarrow C_{23}H_{35}—CO_2H + 2H_2O$

Lithocholic; $C_{23}H_{38}(OH)—CO_2H \longrightarrow C_{23}H_{37}—CO_2H + H_2O$

If the temperature does not exceed 210° (12 mm.), there is anhydride formation (partly to acid-ester, and partly to the neutral anhydride). For example, desoxycholic acid yields an anhydride, $C_{48}H_{78}O_7$, which is capable of reverting to the original acid by hydrolysis.

Cholic acid and desoxycholic acid also become lactonized by heating, a property which is also shown [131] by *iso*lithocholic acid. The ring closure with the latter is represented as follows:



Amino Acids.

Were the amino acids to resemble the hydroxy acids in their thermal decompositions, the position of the amino group should be the determining factor. This is indeed the case, for there are striking similarities between the amino acids and the hydroxy acids.

Corresponding to the lactide formation of the α-hydroxy acids, there is the diketopiperazine formation of the α-amino acids. The α-amino acids have frequently been shown to lose carbon dioxide at elevated temperatures, but the presence of carbon monoxide seems not to have been observed. Only a few β-amino acids have been investigated from this viewpoint, but these cases indicate a very close similarity to the known behavior of the β-hydroxy acids. Unsaturated acids result in both cases. The γ-amino acids form lactams on heating, much as the γ-hydroxy acids form lactones.

[130] Wieland and Weyland, *ibid.* **110**, 138 (1920).
[131] Wieland and Schlichting, *Z. physiol. Chem.* **150**, 267 (1925); Wieland, *ibid.*, **142**, 191 (1925).

α-Amino Acids.

At about 230°, glycine melts with decomposition. This pyrolysis may be controlled by heating glycine in an inert solvent. Balbiano [132] used 10 grams of naphthalene as solvent for 3 grams of glycine, and heated the mixture for 3 hours at 200-204°. After removal of the naphthalene (by solution in benzene, followed by alcohol), a black-colored residue which weighed 2.2 grams indicated a loss of one molecule of water. The residue was capable of reverting to glycine on hydrolysis. Similar, but slower, results were noted by heating glycine in cymene (14 hours at 174°). Assuming that two molecules of water have been eliminated from two of the acid, the following equation expresses this change:

$$2CH_2NH_2—CO_2H \longrightarrow C_4H_6O_2N_2 + 2H_2O.$$

If heated in glycerol at 150-170° (sealed tube), glycine [133] gives diketopiperazine, $\begin{matrix} CH_2—NH—CO \\ | \qquad\qquad | \\ CO—NH—CH_2 \end{matrix}$, as well as a polymeric anhydride, $(C_2H_3ON)_x$.

Glycine may also be heated to give a different type of decomposition. When heated in diphenylamine [134] at 240°, or when boiled vigorously in glycerol,[135] decarboxylation occurs and methyl amine distils away:

$$CH_2NH_2—CO_2H \longrightarrow CH_3NH_2 + CO_2.$$

Similarly, alanine changes by the hot diphenylamine treatment into ethyl amine; and tyrosine, $HO—C_6H_4—CH_2—CHNH_2—CO_2H$, into tyramine (95 percent yield). This conversion of tyrosine into tyramine had also been noted by Waser,[136] who reported a 96 percent yield when heated in fluorene at 280-290°, and a 60-75 percent yield when tyrosine was heated for 30 minutes at 300-310° under diminished pressure.

It seems that the method of heating somewhat determines the course of pyrolysis. This is particularly true with anilidoacetic acid, or phenylglycine, $C_6H_5NH—CH_2—CO_2H$. If rapidly heated,[137] the predominating reaction is one of decarboxylation, and methylaniline, admixed with some primary amine, gradually distils. If gradually heated at 140°, the reaction [138] is one of dehydration, leading to a piperazine derivative in about 70 percent yields.

$$2C_6H_5NH—CH_2—CO_2H \longrightarrow C_6H_5—N\begin{matrix} CH_2—CO \\ \\ CO—CH_2 \end{matrix}>N—C_6H_5 + 2H_2O$$

[132] Balbiano, *Atti. accad. Lincei*, **23**, I, 893 (1914).
[133] Balbiano and Trasciatti, *Ber.* **33**, 2324 (1900); Balbiano, *Ber.* **34**, 1502 (1901).
[134] Abderhalden and Gebelein, *Z. physiol. Chem.* **152**, 125 (1926).
[135] de Coninck and Chauvelt, *Rev. gen. sci.* [7] **8**, 168 (1905).
[136] Waser, *Helv. Chim. Acta* **8**, 758 (1925).
[137] Bischoff and Hausdörfer, *Ber.* **25**, 2271, 2280, 2290, 2298 (1892).
[138] Meyer, *Ber.* **8**, 1156 (1875); *Ber.* **10**, 1967 (1877); Abenius, *Ber.* **21**, 1665 (1888).

The *ortho* and *para* forms of tolyl glycine behave analogously. In this category also are β-naphthyl glycine (but not α-), and α- or β-naphthalido-α-propionic acid, Ar—NH—$CHCH_3$—CO_2H. If α-naphthyl glycine is heated in a current of carbon dioxide at 230°, it changes [139] into the acid anhydride, $(C_{10}H_7NH—CH_2—CO)_2O$. This anhydride-formation is most unusual for monobasic acids. This has been mentioned in another connection on p. 429. Another acid that appears to yield an anhydride by boiling has been recorded [140] by Böttinger:

$$2C_6H_5N{=}CH—CO_2H \longrightarrow (C_6H_5N{=}CH—CO)_2O + H_2O.$$

Methyl Aniline from Phenyl Glycine. Pure methyl aniline is very difficult to prepare by the alkylation of aniline, a fact which is reflected in the very high cost of methyl aniline as compared with that of aniline or of dimethyl aniline. New methods of synthesis are welcomed, therefore, and a study of the pyrolysis of phenyl glycine with this in view has recently been completed [141] by F. W. Johnson. Several distinct features are the outgrowth of this study.

1. Technical phenyl glycine is only very incompletely decarboxylated by heat; the maximum yield of carbon dioxide is 6 percent at 130°, and this value drops to 0.4 percent at 180°. The major course of the reaction is one of dehydration, with the formation of the high-melting diphenyldiketopiperazine.

2. Purified phenyl glycine gives little carbon dioxide below 140°, but the output rises abruptly to 87 percent of the theoretical at 160°, and a maximum of 92 percent at 180°. With phenyl glycine of the highest purity, the elimination of carbon dioxide proceeds slowly at 150° but becomes almost quantitatively expelled after 10-11 hours; at 190°, the decarboxylation is quite rapid and reaches 100 percent of carbon dioxide.

3. These experiments were conducted in the inert solvents: diphenyl ether, naphthalene and diphenyl. The results were found to be almost identical in each case, but diphenyl ether offers the advantage of remaining liquid at room temperature. It has already been mentioned that diphenylamine is also an efficient solvent, and it will be shown that fluorene may also be used.

4. In spite of the high yield of carbon dioxide from pure phenylglycine, no more than 33 percent of methyl aniline could be isolated. This was the case in small runs, and the yield was found to diminish

[139] Bischoff and Nastvogel, *Ber.* **22**, 1808 (1889); Bischoff and Hausdörfer, *Ber.* **25**, 2293 (1892).
[140] Böttinger, *Ann.* **198**, 224 (1879).
[141] Johnson, Dissertation, Northwestern University, 1927.

markedly when larger quantities of phenyl glycine were applied in the same quantity of inert solvent (as was used in the smaller runs).

Diepolder [142] obtained a 46 percent yield of *N*-methyl *o*-anisidine (0.7 gram from 2 grams) by heating *o*-methoxy-phenyl glycine at 170-200°. *N*-Nitroso phenyl glycine becomes decarboxylated [143] in part into nitroso methyl aniline by boiling with water. A misleading observation, and most probably an erroneous one, by Paul [144] stated that *p*-hydroxy-phenyl glycine melts with decomposition between 220-247°, giving carbon dioxide and metol. Neither Ermen nor Harger could duplicate this.[145] Ermen found that methyl amine was evolved instead of carbon dioxide, and that the residue was an intractable tar; if, however, the glycine was heated in a large excess of phenol, then metol and carbon dioxide were liberated by heating, but the method was not a practical one. Johnson [141] also was unable to check Paul's observation, but checked Ermen's. Johnson observed that diphenyl ether could be employed as a solvent to induce the formation of carbon dioxide and *p*-methylaminophenol:

$$HO—C_6H_4—NH—CH_2CO_2H \longrightarrow CO_2 + HOC_6H_4—NHCH_3.$$

With the pure acid, there is only slight decarboxylation below 160°, but it is quickly and completely transformed at 190°. However, only about 30 percent yield of metol can be recovered in such a reaction.

Distillation of *α-o*-toluidino-*iso*valeric acid is stated [146] to yield carbon dioxide and *iso*butyl *o*-toluidine, $CH_3C_6H_4—NH—CH_2—CH(CH_3)_2$. Quick distillation [147] of *α*-anilido-butyric acid yields *n*-propyl aniline, and in general, the reaction:

$$ArNH—CHEt—CO_2H \longrightarrow ArNH—CH_2—Et + CO_2,$$

has been found to apply when *Ar* represents phenyl, *o*- or *p*-tolyl, and *α*- or *β*-naphthyl. Distillation of the corresponding *iso*butyric derivatives, $ArNH—CMe_2—CO_2H$, gives rise to *iso*propyl-aryl-amine (Ar = phenyl and *p*-tolyl). In some of these cases it has been established that piperazine formation is induced by gradual heating (120-180°), and there is no reason to infer that this is not also a general reaction.

Above its melting point, 210-215°, sarkosine [148] changes partly to a dehydration product:

$$2CH_3NH—CH_2CO_2H \longrightarrow CH_3N\begin{<}{}^{CH_2—CO}_{CO—CH_2}\end{>}NCH_3 + 2H_2O,$$

[142] Diepolder, *Ber.* **32**, 3519 (1899).
[143] Fischer, *Ber.* **32**, 249 (1899).
[144] Paul, *Z. angew. Chem.* **10**, 171 (1897).
[145] Harger, *J. Am. Chem. Soc.* **41**, 270 (1919); Ermen, *Photographic Journal* **63**, 223 (1923).
[146] Bischoff, *Ber.* **30**, 2464 (1897).
[147] Bischoff and Mintz, *Ber.* **25**, 2314, 2326 (1892).
[148] Mylius, *Ber.* **17**, 286 (1884).

and partly into dimethyl amine as a result of decarboxylation. *d,l*-Valine, $(CH_3)_2CH—CHNH_2—CO_2H$, gives 3,6-diketo-2,5-di*iso*propyl-piperazine [149] at the melting point. α-Amino*iso*butyric acid,[150] $\begin{matrix}(CH_3)_2C—CO_2H\\ |\\ NH_2\end{matrix}$, loses carbon dioxide by quick heating; otherwise it sublimes at 280° without decomposition. In a sealed tube, its methyl ester changes in part into 3,6-diketo-2,2,5,5-tetramethyl-piperazine.[151] This property of α-amino esters to change smoothly into piperazine derivatives was studied especially by Fischer.[152] Usually, his method was to heat the esters at 160-180° in a sealed tube.

*Iso*amyl amine results [136] when either leucine or its barium salt is heated. The yield of amine [152a] may be made quantitative if leucine is added to petroleum or to fluorene at 120°, following which the temperature is rapidly raised to 200-235°:

$$(CH_3)_2CH—CH_2—CHNH_2—CO_2H \longrightarrow CO_2 + (CH_3)_2CH—CH_2—CH_2NH_2.$$

When leucine is heated alone, not only *iso*amyl amine, but also *iso*butyl cyanide and 3,6-diketo-2,5-di*iso*butyl-piperazine are formed. The presence of these compounds is especially noteworthy since they reveal a relationship between the α-hydroxy acids and the α-amino acids.

It will be recalled (p. 426) that α-hydroxy-*iso*caproic acid pyrolyzes first to the lactide, and finally into *iso*valeric aldehyde:

$$2R—CHOH—CO_2H \longrightarrow R—CH\begin{matrix}O—CO\\ \diagup\quad\diagdown\\ CO—O\end{matrix}CH—R \longrightarrow 2RCHO + 2CO.$$

(R = *iso*butyl)

To behave analogously, leucine should form the piperazine derivative, which it does; but also, it should form an ammono-aldehyde, which it has not been observed to do:

$$2R—CHNH_2—CO_2H \longrightarrow R—CH\begin{matrix}NH—CO\\ \diagup\quad\diagdown\\ CO—NH\end{matrix}CH—R,$$

but not $2RCH{=}NH + 2CO$. Experience with the thermal decomposition of amines (p. 290), however, leads us to believe that these ammono-aldehydes, R—CH=NH, are unstable at elevated temperatures, since nitriles are always isolated in their stead. *Iso*butyl cyanide,

[149] Fischer and Schenkel, *Ann.* **354**, 20 (1907).
[150] Tiemann and Friedlaender, *Ber.* **14**, 1972 (1881).
[151] Franchimont and Friedmann, *Rec. trav. chim.* **27**, 197 (1908).
[152] Fischer, *Ber.* **34**, 435 (1901); **38**, 4180 (1905); **39**, 557 (1906).
[152a] Keimatsu and Yamamoto, *Chem. Abstracts* **22**, 944 (1928).

R—CN, which was isolated is, therefore, excellent evidence for the transitory existence of the ammono-aldehyde, RCH=NH.

The decarboxylation reaction which occurs [153] in the dry distillation of cystine, $(—S—CH_2—CHNH_2—CO_2H)_2$, leads to the formation of β,β-diamino-diethyl-disulfide, $(—S—CH_2—CH_2NH_2)_2$. At 260°, in a sealed tube, betaine hydrochloride [154] decomposes largely into trimethyl-ammonium chloride and carbon dioxide:

$$(CH_3)_3NCl—CH_2—CO_2H \longrightarrow (CH_3)_4NCl + CO_2.$$

Dipeptides. One would suspect that dipeptides should change into the 2,5-diketopiperazines more easily than the comparable α-amino acids. Usually, this effect is produced with dipeptides by fusion. To illustrate: [155]

$$HN\!<\!\begin{matrix}CH(CH_3)—CO_2H\\ CO—CH(CH_3)—NH_2\end{matrix} \longrightarrow HN\!<\!\begin{matrix}CH(CH_3)—CO\\ CO—CH(CH_3)\end{matrix}\!>\!NH + H_2O$$

$$HN\!<\!\begin{matrix}CHEt—CO_2H\ [156]\\ CO—CHEt—NH_2\end{matrix} \xrightarrow{275°} HN\!<\!\begin{matrix}CHEt—CO\\ CO—CHEt\end{matrix}\!>\!NH + H_2O.$$

Tyrosylproline, $C_{14}H_{18}N_2O_4$, is gradually converted [157] into an anhydride at 105-110°. This anhydride, melting point 187°, may be hydrolyzed to an enol isomer of the original tyrosylproline by barium hydroxide, and this enol isomer loses water at 180° to form a second anhydride, melting point 226°. *d,l*-Leucylglycine gives a 93 percent yield of the enolic form [158] of leucylglycine anhydride by heating it to 240° in diphenyl-amine. Other similar cases of the formation of 2,5-diketopiperazines are as follows: leucyl-valine, 90 percent of the enolic anhydride; alanyl-valine, 96 percent; leucyl-leucine, 93.6 percent; α-aminobutyryl-α-amino-butyric acid, 98 percent, and α-amino*iso*butyryl-α-amino*iso*butyric acid, which is theoretically incapable of forming an enolic anhydride, 89.7 percent of the keto-anhydride. It is interesting to note [159] that the enol form of 2,5-diketopiperazines reacts with ozone, whereas the keto form does not.

α-Amino phenylacetic acid sublimes [160] at 256° without melting, but decomposes smoothly by distillation [161] into carbon dioxide and benzyl amine. This behavior is dissimilar to that of the corresponding α-hydroxy

[153] Neuberg and Ascher, *Chem. Zentr.* **1907**, II, 1156.
[154] Stanek, *Chem. Zentr.* **1903**, II, 24.
[155] Fischer, *Ann.* **340**, 126 ff. (1905).
[156] Fischer and Raske, *Ann.* **340**, 187 (1905).
[157] Abderhalden and Sickel, *Z. physiol. Chem.* **153**, 16 (1926).
[158] Abderhalden and Gebelein, *ibid.* **152**, 125 (1926).
[159] Abderhalden and Schwab, *ibid.* **157**, 140 (1926).
[160] Elbers, *Ann.* **227**, 344 (1885).
[161] Tiemann and Freidlaender, *Ber.* **14**, 1969 (1881).

compound, mandelic acid (p. 429). Amino diphenylacetic acid, corresponding to benzilic acid, seems not to have been synthesized.

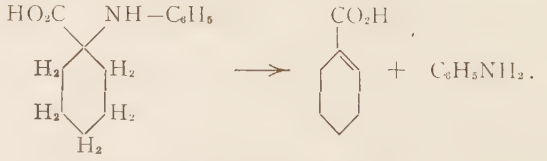
*Iso*amylamino phenylacetic acid [162] also loses carbon dioxide by dry distillation:

$$C_6H_5—\underset{\displaystyle NH—C_5H_{11}}{\underset{|}{CH}}—CO_2H \longrightarrow C_6H_5—CH_2—NHC_5H_{11} + CO_2.$$

Anilino phenylacetic acid,[163] $C_6H_5—CH(NHC_6H_5)—CO_2H$, gives a little benzyl aniline (about 5 percent by quick heating), but it gives considerably more aniline and it also gives rise to a large quantity of resinous products. Since benzyl aniline changes into acridine, and not into aniline, by pyrolysis (pp. 102 and 295), aniline must have been formed from the original amino acid. Whether or not this case parallels that of mandelic acid cannot be stated, since the resinous product was not investigated.

Esters of this type of α-amino acid appear to behave normally, since diphenyl-diketo-piperazine, $C_6H_5CH\begin{matrix}CO—NH\\NH—CO\end{matrix}CHC_6H_5$, is formed [164] by long heating of methyl aminophenylacetate, $C_6H_5—CHNH_2—CO—OCH_3$.

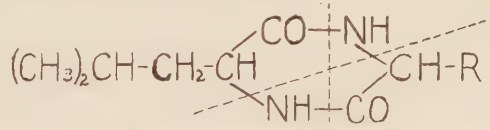
By heating α-ethylamino-γ-phenyl-butyric acid [165] at 230° in fluorene, there is formed an 80 percent yield of ethyl-phenylpropyl-amine. A similar decarboxylation of the amylamino derivative, $C_6H_5—CH_2CH_2CH(NHC_5H_{11})—CO_2H$, gives a 70 percent yield of amyl-phenylpropyl-amine. A somewhat different course is encountered in the case [166] of 1-anilino-cyclohexane-1-carboxylic acid. If this is distilled from a flask, an oily distillate of aniline and Δ^1-cyclohexene-1-carboxylic acid is formed in contrast to the decarboxylation reactions which have just been mentioned:



Ovalbumin and Silk Fibroin. The gradual distillation (70-350°) of ovalbumin [167] under diminished pressure gives water, 30 percent;

[162] Einhorn and Pfeiffer, *Ann.* **310**, 220 (1900).
[163] Tiemann and Piest, *Ber.* **15**, 2031 (1882).
[164] Kossel, *Ber.* **24**, 4149 (1891).
[165] Skita and Wulff, *Ann.* **455**, 17 (1927).
[166] Betts, Muspratt and Plant, *J. Chem. Soc.* **1927**, 1310.
[167] Pictet and Cramer, *Helv. Chim. Acta* **2**, 288 (1919).

coke, 32 percent; organic matter, entirely soluble in ether, 15 percent; gases and loss, 23 percent. The organic matter consists of both acidic and basic substances, the former including acetic, propionic, butyric and succinic acids. An amine, thought to be dihydroaniline, is present in the basic portion. The neutral portion of the distillate consists of fairly large amounts of *iso*capronamide, $(CH_3)_2CH—CH_2—CH_2CONH_2$, and small quantities of acetamide, propionamide and indole. These authors consider such amides to be the precursors of nitriles, which have been noticed in protein distillation. This is in contrast to the older view [168] of their genesis, which assumed interaction of amines with fatty acids. Pictet and Cramer adopt the diacipiperazine linkage of amino acids in proteins, and postulate that the amide (*iso*capronamide) may not necessarily be derived from leucine, but that both of these compounds may result from the same molecular grouping in the albumin complex. This speculation is expressed in the formula:



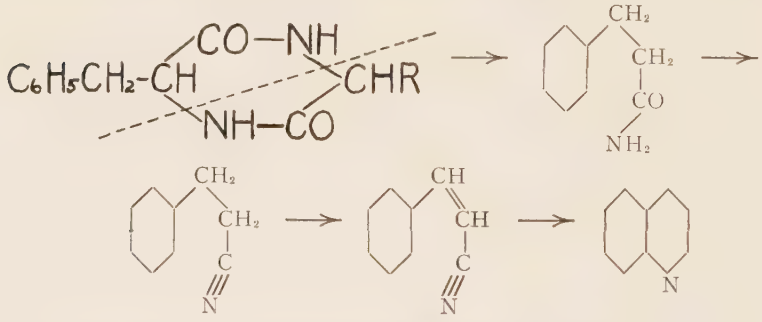
which may undergo cleavage in one of the two suggested ways giving leucine or *iso*capronamide. Such a mechanism has also been tentatively postulated [169] by Johnson and Daschavsky to explain results of the pyrolysis of silk fibroin, which will be presented shortly.

The results of research on protein distillation up to 1885 are included in the short contributions [170] by Limpricht and Williams, and a series of papers by Wiedel [171] and his co-workers, in which is reviewed the previous work on bone oil and glue. In this connection it may be stated that pyridine and picolines are found both in coal tar and in bone tar, but to a greater extent in bone tar. By the dry distillation of bones [172] in a horizontal iron retort (preferred to a vertical one) at a cherry-red heat, there is formed bone charcoal in 68-70 percent yields, bone oil 5.3-6.8 percent, ammoniacal liquor 17-18 percent, and fuel gases 5-8 percent. The bone charcoal prepared in this way is stated to possess unusual catalytic activity, inducing hydrogen and oxygen to react at room temperatures, as well as chlorine and acetylene.

Destructive distillation [169] of silk fibroin in a large iron pipe, heated on an ordinary combustion furnace, leaves a residue of silk-coke or

[168] Wiedel and Ciamician, *Ber.* **13**, 65 (1880).
[169] Johnson and Daschavsky, *J. Biol. Chem.* **62**, 197 (1924); *J. Am. Chem. Soc.* **41**, 1147 (1919).
[170] Limpricht, *Ann.* **101**, 297 (1857); Williams, *Ann.* **109**, 127 (1859).
[171] Wiedel and others, *Monatsh.* **1**, 279 (1880); **5**, 656 (1884).
[172] Alekseevskii, *J. Russ. Phys. Chem. Soc.* **53**, 306 (1921); *Chem. Abstracts* **17**, 3235 (1923).

amorphous carbon, amounting to 41 percent of the total. In the red oily distillate are phenol, *p*-cresol, indole, quinoline, ammonia, methyl and perhaps ethyl amine, pyrrole, acetic acid and propionic acid. Carbon dioxide is evolved. To explain these products, Johnson suggests that phenol and cresol result from a breakdown of the tyrosine in fibroin, cresol being the precursor of phenol. Indole is conceivable as a degradation product of tryptophane, but these authors point out the inadequacy of such a statement since tryptophane appears to be absent in silk fibroin. It is present, however, in ovalbumin. Possibly indole is formed as a result of a secondary reaction at high temperatures. At least, Pictet and Cramer showed that indole may be formed by passing alkylated anilines through a hot tube. Quinoline formation is also difficult to explain, except through secondary reactions, inasmuch as there is no conclusive evidence that the quinoline nucleus functions as such in the fibroin molecule. Johnson and Daschavsky suggest the following provisional explanation for the presence of quinoline:



Phenyl alanine, which has been shown to be present in fibroin, may be assumed to occur in the cyclic form. It then is considered to undergo cyclic cleavage as indicated, followed by dehydration, dehydrogenation, and rearrangement into quinoline.

The formation of the aliphatic amines was considered to be the result of decarboxylation of *α*-amino acids, and the fatty acids were thought to be formed by reduction of the fatty acids:

$$\mathrm{R{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CO_2H} + 2H \longrightarrow \mathrm{R{-}CH_2{-}CO_2H} + NH_3.$$

Leather Scrap, Glue, Etc. The destructive distillation of collagenous materials, such as glue, gelatine or leather scrap, is recommended [173] as the best way to prepare pyrroles and pyrocoll. Pyrocoll

[173] Michelmann, *Ind. Eng. Chem.* **17**, 471 (1925); Brit. Pat. 231,888, Apr. 3, 1924; U. S Pat. 1,572,552; *Chem. Abstracts* **19**, 3614 (1925); **20**, 1336 (1926); Blicke and Powers, *Ind. Eng. Chem.* **19**, 1334 (1927).

crystals may be obtained from the oily condensate by adding such a diluent as toluene. It appears that better yields are obtained from chrome tanned leather than from the vegetable tanned product. Blicke and Powers question the value of Michelman's process for pyrrole formation, since no yields are given and since the process of purification must be tedious.

Ketene-nitrones. A curious class of compounds, which are formed by the addition of diphenyl ketene to nitrones, $Ar_2C{=}N{-}Ar$ (O), may be discussed with α-amino acids, since the structure of these compounds, $Ar_2C(Ar){-}N(O{-}CO){-}C(C_6H_5)_2$, is related to the inner-salt structure of α-amino acids, $H_3N{-}CHR(O{-}CO)$. Quite generally, carbon dioxide is eliminated [174] and a nitrene, $Ar_2C{=}N{=}C(C_6H_5)_2$ (Ar), is produced. This decomposition occurs at 190° with diphenylketene-diphenyl-*N*-phenyl-nitrone:

$$(C_6H_5)_2C{=}N(C_6H_5){-}C(C_6H_5)_2 \longrightarrow (C_6H_5)_2C{=}N(C_6H_5){=}C(C_6H_5)_2 + CO_2.$$

(O———CO)

The corresponding diphenylketenediphenyl-*N*-*p*-tolyl-nitrone undergoes pyrolysis in this manner at 170°, and the -*N*-*p*-dimethylaminophenyl-nitrone at 180°. The yields of nitrenes are good. About 75 percent of the theoretical amount of carbon dioxide is evolved as diphenylenediphenyl-*N*-phenyl-nitrene, $(C_6H_4)_2C{=}N(C_6H_5){=}C(C_6H_5)_2$, is prepared from diphenylketenediphenylene-*N*-phenyl-nitrone. The addition product of phenyl-*N*-phenylnitrone, $C_6H_5CH{=}N(C_6H_5)(O)$, and diphenylketene decomposes similarly at 215° into triphenyl-*N*-phenylnitrene, $C_6H_5CH{=}N(C_6H_5){=}C(C_6H_5)_2$.

*Iso*cyanates, which frequently are so similar to ketenes, behave analogously in this reaction. Phenyl *iso*cyanate forms an addition product with diphenyl-*N*-phenyl-nitrone, giving $C_{26}H_{20}O_2N_2$, presumably $(C_6H_5)_2C{-}N(C_6H_5){-}N{-}C_6H_5$ (O———CO). Fifty percent of the theoretical amount of carbon dioxide is evolved by heating it one hour at 210°.

[174] Staudinger and Miescher, *Helv. Chim. Acta* **2**, 554 (1919).

β-Amino Acids.

Above its melting point, 196-206°, β-aminopropionic acid [175] yields ammonia and acrylic acid:

$$H_2N{-}CH_2{-}CH_2{-}CO_2H \longrightarrow NH_3 + CH_2{=}CH{-}CO_2H .$$

β-Anilinobutyric acid, $CH_3{-}\underset{\displaystyle NHC_6H_5}{\underset{|}{CH}}{-}CH_2{-}CO_2H$, yields [176] aniline and crotonic acid by vacuum distillation. This reverses the method of preparation, since β-anilinobutyric acid is easily formed from aniline and crotonic acid in the presence of ultraviolet light. A similar pyrolysis of β-phthalimido-β-phenylpropionic acid occurs [177] on heating at 320-350° for half an hour:

$$C_6H_5{-}\underset{\displaystyle N{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4}{\underset{|}{CH}}{-}CH_2{-}CO_2H \longrightarrow C_6H_5CH{=}CH{-}CO_2H + C_6H_4\begin{smallmatrix}CO\\ \diagup\ \diagdown\\ NH\\ \diagdown\ \diagup\\ CO\end{smallmatrix} .$$

Above 240°, carbon dioxide is evolved, and the odor of styrene is noticeable (see p. 349 for the pyrolysis of cinnamic acid).

Interest is attached to these decompositions because of their similarity to the pyrolyses of β-hydroxy acids, emphasizing again that the amino group and the hydroxyl group are more or less interchangeable so far as the reaction mechanism of pyrolysis is concerned. It would be expected that β-anilido-*iso*butyric acid [178] should give aniline by distillation and such is the case. However, instead of the formation of methacrylic acid there is produced a lactone, melting point 120°, which is apparently formed by interaction of β-anilido-*iso*butyric acid and methacrylic acid:

$$C_6H_5NH{-}CH_2{-}CHMe{-}CO_2H \longrightarrow C_6H_5NH_2 + [CH_2{=}CMe{-}CO_2H]$$

$$C_6H_5{-}NH{-}CH_2{-}CHMe{-}CO_2H + [CH_2{=}CMe{-}CO_2H] \longrightarrow H_2O +$$

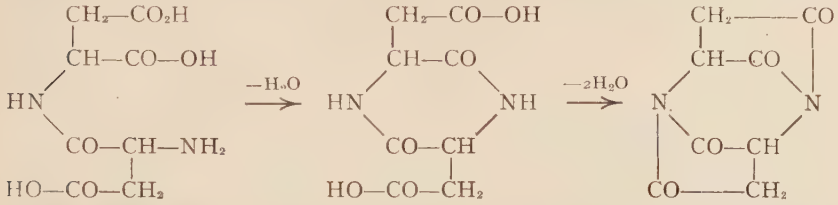
$$\left[\begin{smallmatrix}CH_2{-}CHMe{-}CO_2H\\ |\\ C_6H_5N{-}CO{-}CMe{=}CH_2\end{smallmatrix}\right] \longrightarrow \begin{smallmatrix}CH_2{-}CHMe{-}CO\\ |\qquad\qquad >O\\ C_6H_5N{-}CO{-}C(CH_3)_2\end{smallmatrix}$$

The β-*o*- and the β-*p*-toluido-*iso*butyric acids behave analogously. The naphthalido derivatives have also been studied.

The dipeptide of aspartic acid behaves like other dipeptides (p. 463) and becomes dehydrated at 210°. Thus, the β-amino group is not eliminated in the manner of simple β-amino acids. Three molecules of water

[175] Mulder, *Ber.* **9**, 1904 (1876).
[176] Stoermer and Robert, *Ber.* **55**, 1030 (1922).
[177] McKenzie and Barrow, *J. Chem. Soc.* **119**, 69 (1921).
[178] Bischoff and Mintz, *Ber.* **25**, 2331, 2334, 2345 (1892).

are lost, but presumably the first effect is the formation of a piperazine derivative, later to be followed by two γ-ring closures:



The ultimate anhydride reverts [179] to the original dipeptide by hydrolysis with barium hydroxide. *l*-Aspartic acid itself is dehydrated [180] to polyaspartides and polyaspartic acids if maintained at 190-200° for a long time.

In the dry distillation [181] of *dl*-α,β-diaminopropionic acid, the effect is one of decarboxylation. α-Amino acids have been shown (p. 459) to behave in this manner. Ethylene diamine is formed:

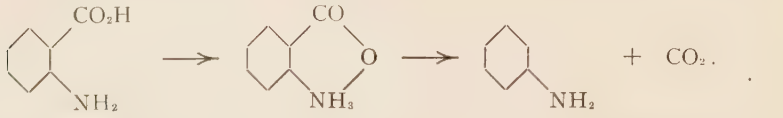
$$CH_2NH_2—CHNH_2—CO_2H \longrightarrow CH_2NH_2—CH_2NH_2 + CO_2.$$

Other diamines have been prepared similarly, and this method for their synthesis has been highly recommended. Above 300°, α,α'-diaminosebacic acid changes into octamethylenediamine; hexamethylene-diamine is similarly produced by the dry distillation of α,α'-diaminosuberic acid. In these pyrolyses, there is no tendency for ring closure to cyclic imines, $(CH_2)_n{=}NH$, but this tendency would undoubtedly have appeared if the dihydrochlorides had been heated (p. 325) instead of the free amino acids. In fact, Schulze and Winterstein [182] obtained small amounts of pyrrolidine and not putrescine after the dry distillation of the hydrochloride of diaminovaleric acid.

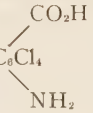
Anthranilic acid and related compounds represent another type of β-amino acid, the type wherein the α- and β-carbon atoms are part of an aromatic nucleus. In these cases, decarboxylation alone is encountered. The nitrogen is never eliminated as ammonia. In hot glycerol, carbon dioxide is expelled [183] from *o*-aminobenzoic acid, whereas the *meta,* and especially the *para,* isomers remain unchanged. In water at 100°, however, both the *o*- and *p*-isomers [184] change into aniline and carbon dioxide, but the *ortho* isomer decomposes twice as fast. The *meta* compound is stable under these conditions. McMaster and Shriner sug-

[179] Ravenna and Bosinelli, *Atti. accad. Lincei,* **28**, II, 113 (1919).
[180] Schiff, *Ber.* **30**, 2449 (1897); *Ann.* **303**, 183 (1898); **307**, 231 (1899).
[181] Neuberg and Niemann, *Z. physiol. Chem.* **45**, 92, 110, 120 (1905).
[182] Schulze and Winterstein, *Ber.* **32**, 3193 (1899).
[183] de Coninck and Chauveult, *Rev. gen. chim.* [7] **8**, 168 (1905).
[184] McMaster and Shriner, *J. Am. Chem. Soc.* **45**, 751 (1923).

gest inner salt formation as the determining factor for the ease of decomposition. Thus:

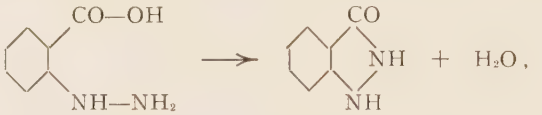


In the absence of solvents, anthranilic acid undergoes pyrolysis above its melting point into carbon dioxide [185] and aniline.[186] The decomposition is complete in one hour [187] at 205-210°. This decomposition of the amino-benzoic acids (*ortho, meta,* and *para*) above their melting points was observed to be a troublesome factor [188] in the determination of their heat capacities. Above its melting point, 182°, tetrachloro-



anthranilic acid, C_6Cl_4 , passes [189] into 2,3,4,5-tetrachloroaniline.

Contrasting with this behavior is the thermal dehydration (not decarboxylation) of *o*-hydrazinobenzoic acid [190] into indazolone:

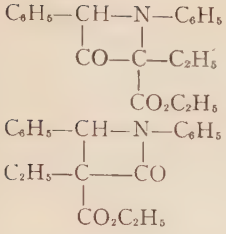


but it is well to point out that the *o*-amino acids and the *o*-hydrazino acids are not strictly comparable, since the latter may undergo a 5-membered ring closure. *o*-Hydrazino-benzoic acid is, therefore, more analogous to the γ-amino acids.

β-Lactams are never formed as thermal decomposition products of β-amino acids; neither were β-lactones ever observed from β-hydroxy acids. Staudinger [191] has prepared β-lactams by the addition of ketene to Schiff's bases. Thus, at 180-200°, ketene attaches itself to benzylidene aniline forming β-anilino-β-phenylpropionic lactam. At 600°, this undergoes pyrolysis into phenyl *iso*cyanate and styrene:

If ethyl ketene carboxylic ester is used in the above reaction, it forms an addition product at $-20°$ giving the unstable compound,

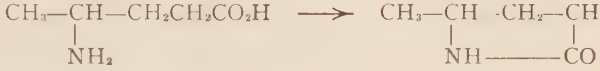
[185] Fritzsche, *Ann.* **39**, 86 (1841).
[186] Liebig, *ibid.* p. 94.
[187] Powlewski, *Ber.* **37**, 592 (1904).
[188] Andrews, Lynn and Johnston, *J. Am. Chem. Soc.* **48**, 1282 (1926).
[189] Villiger and Blaugey, *Ber.* **42**, 3552 (1909).
[190] Fischer, *Ber.* **13**, 681 (1880); *Ann.* **212**, 333 (1882).
[191] Staudinger, *Ber.* **50**, 1035 (1917).



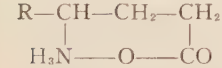
which at 200° rearranges to the β-lactam,

γ-Amino Acids.

The tendency for γ-hydroxy acids to form lactones is reflected in the tendency for γ-amino acids to form lactam . In both cases, water is eliminated, but usually it is far easier to produce lactones than lactams. Whereas γ-hydroxybutyric acid is stable only at very low temperatures, γ-aminobutyric acid is a fairly stable compound. It melts with decomposition between 193-202°, giving water and pyrrolidone.[192] Its homolog, γ-amino-*n*-valeric acid similarly pyrolyzes [193] into methyl-2-pyrrolidone-5 by distillation:

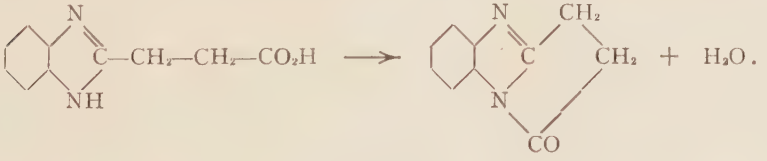


Such changes presumably are preceded by salt formation,



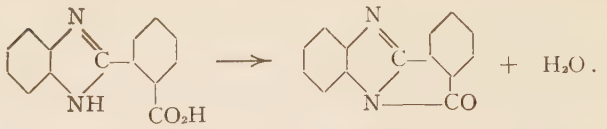
in which event the reaction is strikingly similar to amide formation, such for example as acetamide from ammonium acetate.

Benzimidazole-propionic acid [194] undergoes a pyrrolidone ring closure at 230° (oil bath temperature) and forms propionylene benzimidazole as a sublimation product:

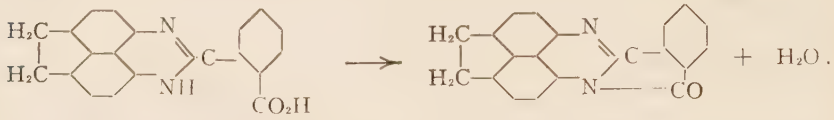


This change is very similar to that of 2-phenyl-benzimidazole-*o*-carboxylic acid, which yields [195] *o*-benzoylene-benzimidazole at 280-290° (in 15 minutes):

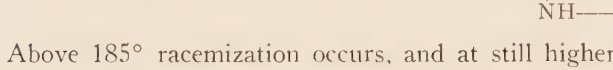
[192] Gabriel, *Ber.* **22**, 3338 (1889).
[193] Tafel, *Ber.* **19**, 2415 (1886); **22**, 1860 (1889).
[194] Meyer and Lüders, *Ann.* **415**, 42 (1918)
[195] Thiele and Falk, *Ann.* **347**, 129 (1906).



Again, the change of aceperimino-*o*-benzoic acid [196] to its dehydration product, phthalo-aceperinone, occurs at 80°:

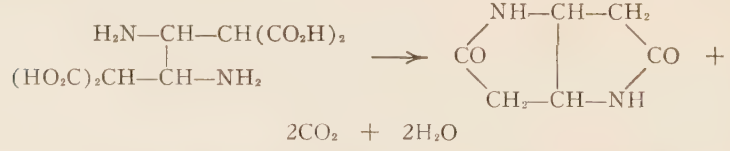


Glutamic acid is both an α- and a γ-amino acid. The γ-ring closure is effected by heating [197] at 180-190° for 2-3 hours, or at 150-160° for four hours,[198] or by heating 2 hours at 150-165° followed by 15 minutes at 180°. At the lower temperature, *d*-glutamic acid gives *l*-pyrrolidone carboxylic acid, and the *l*-acid forms the *d*-lactam:



Above 185° racemization occurs, and at still higher temperatures, dry distillation takes place and pyrrole is produced among other substances. Unnecessarily long heating is also to be avoided.

β,β'-Diamino-α-α'-dicarboxyadipic acid behaves [199] as a γ,γ'-diamino acid, as well as a derivative of malonic acid. The dilactam of β,β'-diaminoadipic acid is produced at about 180°:

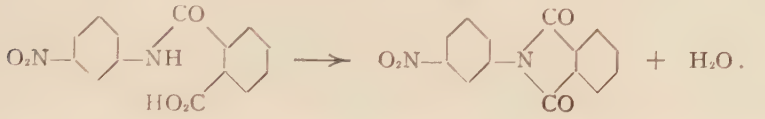


The heating of β-(α-piperidyl)-propionic acid [200] (also called pelletierinic acid) induces a similar type of change, and produces the bicyclic 2-piperolidone:

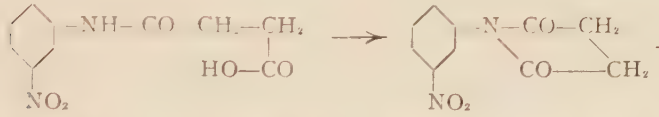
The presence of a carbonyl group in the chain does not prevent the 5-membered ring closure by thermal means. Anils, instead of lactams,

[196] Sachs and Mosebach, *Ber.* **44**, 2861 (1911).
[197] Abderhalden and Kautzsch, *Z. physiol. Chem.* **64**, 447 (1190); **68**, 487 (1910).
[198] Skola, *Z. Zuckerind. cechoslav. Rep.* **44**, 347 (1920); *Chem. Abstracts* **15**, 525 (1921).
[199] Traube, *Ber.* **35**, 4124 (1902).
[200] Löffler and Kaim, *Ber.* **42**, 99 (1909).

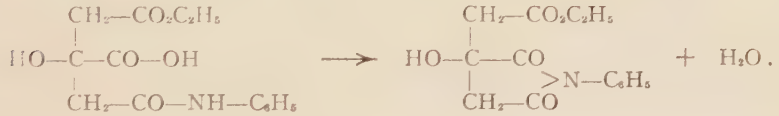
are the products formed. *m*-Nitrophthalanilic acid,[201] if heated rapidly, melts with foaming at 202°, and then resolidifies, later to melt at 240°, which is the melting point of *m*-nitrophthalanil:



The *o*- and *p*-nitro isomers behave similarly if kept at 200° for half an hour, as does also *m*-nitrosuccinalic acid:



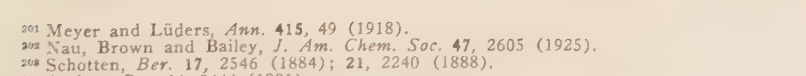
The case of ethyl citranilide[202] is parallel. It melts at 108°, and fifty degrees higher changes into ethyl citranilate:



δ-Amino Acids.

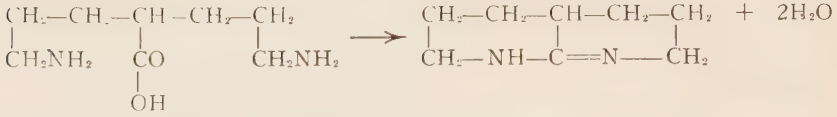
In marked similarity to the manner in which γ-amino acids form 5-membered rings, the δ-amino acids form 6-membered heterocyclic rings. This change usually occurs at the melting point, or by vacuum distillation. To illustrate: piperidone is formed[203] by fusion of δ-amino-valeric acid (158°):

Its α-methyl homolog, $H_2N{-}CH_2CH_2CH_2{-}CH(CH_3){-}CO_2H$, melts[204] with decomposition at 168°, yielding β-methyl-α-piperidone. α-Aminoadipic acid, which behaves as a δ-amino acid towards heat, yields α-piperidone-α′-carboxylic acid[205] at its melting point, 206°:



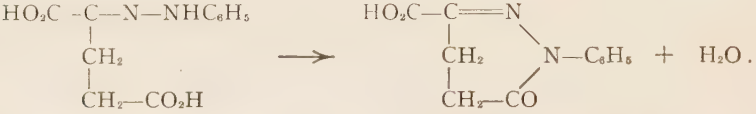
[201] Meyer and Lüders, *Ann.* **415**, 49 (1918).
[202] Nau, Brown and Bailey, *J. Am. Chem. Soc.* **47**, 2605 (1925).
[203] Schotten, *Ber.* **17**, 2546 (1884); **21**, 2240 (1888).
[204] Aschan, *Ber.* **24**, 2444 (1891).
[205] Dieckmann, *Ber.* **38**, 1654 (1905).

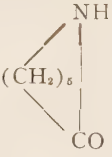
A slight modification is encountered in the change of bis-γ-aminopropylacetic acid [206] into the octahydride of 1,8-naphthyridin, which occurs by distillation. In this case, the carboxyl group shares itself with two δ-amino groups to form a bicyclic compound.



This is an excellent illustration of the pronounced tendency for water elimination in δ-amino acids.

The pyrolytic transformation [207] of the phenylhydrazone of α-ketoglutaric acid into 1-phenyl-6-pyridazinone-3-carboxylic acid again illustrates the strong tendency for a 6-membered ring closure:



Seven membered rings have also been formed by the pyrolysis of amino acids, but far less smoothly. ε-Aminocaproic acid [208] forms its lactam,  , in but 20-30 percent yields by heating, whereas the remainder is polymerized into a tough resin. Analogously, α-aminopimelic acid, $HO_2C—CHNH_2—(CH_2)_4—CO_2H$, changes [205] in part into the 7-membered lactam, but the major product is an ill-defined product of high molecular weight.

Scarcely any of the 8-membered lactam is produced [209] by heating 7-aminoheptanoic acid, $H_2N—(CH_2)_6—CO_2H$. An amorphous substance is formed instead.

[206] Reissert, *Ber.* **26**, 2137 (1893); **27**, 979 (1894).
[207] Wislicenus and Waldmüller, *Ber.* **44**, 1564 (1911).
[208] Gabriel and Mass, *Ber.* **32**, 1271 (1899).
[209] Manasse, *Ber.* **35**, 1370 (1902).

CHAPTER 16.

SALTS OF ORGANIC ACIDS.

Formates and Oxalates.

A well known industrial preparation of sodium oxalate depends on the pyrolysis [1] of sodium formate:

$$2H—CO_2Na \longrightarrow H_2 + (CO_2Na)_2.$$

At 440°, the reaction [2] is completed in five minutes, giving about 53 percent yield. The presence of 2 percent of sodium hydroxide increases this yield to 83 percent. Contardi [3] gives a discussion of the various patented processes for this reaction.

In a study of the best conditions [4] for the transformation of sodium formate into sodium oxalate, Leslie and Carpenter recommend the presence of 1 percent of sodium hydroxide, a temperature of 350°, and a pressure of 14 inches of mercury. To avoid the danger of explosion, the reaction should be continuous and sodium formate should be added gradually into the heated zone. In general, increased yields are favored by an increase in temperature, but since sodium oxalate, which is desired, starts to undergo pyrolysis into sodium carbonate [5] even at 160°, it is obvious that an optimum temperature should be used in this decomposition. This, according to Leslie and Carpenter, is about 350°, at which temperature yields approaching 90 percent may be realized commercially. Sodium carbonate, in the decomposition products, may be explained by one of the two reactions:

$$Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO,$$

or

$$H—CO_2Na + NaOH \longrightarrow H_2 + Na_2CO_3.$$

Possibly the oxalate is an intermediate product in the pyrolysis of other metallic formates, but oxalates are never formed in appreciable amounts except for sodium or potassium formate. The carbonate (or oxide) is the customary residue. Usually also, there is a liquid distillate

[1] Dumas and Stas, *Ann.* **35**, 138 (1840); Merz and Weith, *Ber.* **15**, 1507 (1882).
[2] Matignon and Marchal, *Bull. soc. chim.* **31**, 789 (1922).
[3] Contardi, *Giorn. chim. ind. applicata* **5**, 3 (1922); *Chem. Abstracts* **17**, 2106 (1923).
[4] Leslie and Carpenter, *Chem. Met. Eng.* **22**, 1195 (1920).
[5] Ott, *Z. physik. Chem.* **109**, 1 (1924).

composed of such organic substances as methyl formate, formaldehyde, methanol, acetone, etc.

Traces of calcium oxalate may be detected in the residue of calcium carbonate which results [6] when calcium formate is decomposed at 420-430° in an aluminum apparatus. The 2 gram-atoms of carbon which exist in one gram-molecule of calcium formate were distributed as follows after the decomposition: 1.02 gram-atoms in the residue (largely $CaCO_3$), 0.54 gram-atom in the gas (which contained 47.9 percent carbon monoxide, 23.8 percent hydrogen and 2 percent methane), 0.20 gram-atom of carbon as methanol, 0.13 gram-atom of carbon as an oily distillate, and 0.11 gram-atom of loss or carbonization. By carrying out the decomposition in a current of steam, these authors reported a 52 percent yield of methanol.

Vignon's results [7] are quite different, especially with regard to the ratio of carbon monoxide to hydrogen. He heated calcium formate at 360-370°. According to Vignon, the gases, by volume, are: carbon dioxide, 20 percent; carbon monoxide, 27 percent; hydrogen, 51 percent; and methane, 2 percent. Vignon's main thesis in this connection was a study of the interaction of carbon monoxide with lime. He found that no gaseous products are evolved until 350°. At 400°, methane, ethylene and hydrogen come off quite readily, and above 400° the ratio of hydrocarbons to hydrogen diminishes till at 600° the gas is almost exclusively hydrogen. To explain these results, therefore, he set up the following equations:

$$2CO + Ca(OH)_2 \longrightarrow Ca(O{-}CO{-}H)_2 \longrightarrow H_2 + CaC_2O_4$$

$$CaC_2O_4 \longrightarrow CaCO_3 + CO,$$

and,

$$2Ca(O{-}CO{-}H)_2 + CaO \longrightarrow 3CaCO_3 + CH_4,$$

or,

$$4Ca(O{-}CO{-}H)_2 + 2CaO \longrightarrow 6CaCO_3 + C_2H_4 + 2H_2.$$

To secure evidence for the latter two equations, Vignon heated mixtures of calcium formate and calcium oxide at 340°. The results are given in Table XLIII.

TABLE XLIII. *Pyrolysis of Calcium Formate-Lime Mixtures.*

	$Ca(O{-}CO{-}H)_2 + CaO$	$Ca(O{-}CO{-}H)_2 + 2CaO$
	Percent	Percent
Carbon monoxide	40	26
Hydrogen	30	42
Carbon dioxide	6	0
Hydrocarbons (as methane)	24	32

[6] Fischer, Tropsch and Schellenberg, *Ges. Abhandl. Kenntnis Kohle* **6**, 330 (1921); *Chem. Abstracts* **18**, 3170 (1924).

[7] Vignon, *Ann. chim.* [9] **15**, 55 (1921).

Fischer's studies [8] included not only calcium formate, but also the pyrolysis of barium, magnesium and lithium formates. Barium formate froths considerably (aluminum apparatus) at 350-375°, and from 45.4 grams of the salt, 2.2 grams of methanol was isolated. The gas which is evolved contains no methane and no unsaturated hydrocarbons. Magnesium formate, if pyrolyzed at 400-425°, gives an aqueous distillate. About two-thirds of the carbon content is present either in the residue or in the gas. Lithium formate breaks down at 350° giving lithium carbonate and an alcoholic distillate, but no oil.

Organic liquids also appear when stannous formate is heated. This decomposition occurs below 180°, and may, as suggested,[9] be in accordance with the following equation, but probably there are more fundamental changes involved:

$$3(H{-}CO_2)_2Sn \longrightarrow 3SnO + 3CO_2 + H{-}CHO + H{-}CO_2CH_3.$$

The temperature [10] at which a distinct and sustained evolution of gas begins from formates is in general higher the more basic is the metallic oxide. These decomposition temperatures are given in Table XLIV.

TABLE XLIV. *Decomposition Temperatures of Metallic Formates.*

Metallic Oxide	Temperature °C.	Metallic Oxide	Temperature °C.
Cu^{++}	170	UO_2	317
Pb	200	Ba	335
Ni	210	Mg	340
Zn	240	Sr	355
Fe^{++}	250	Li	355
Mn	300	Na	355
		K	375

In a rather extended investigation with the pyrolysis of several metallic formates, Hofmann provides an explanation [11] for the diversified array of experimental data, if it is accepted that the first step is displacement of hydrogen atoms within the molecule. There are four different ways by which this may be accomplished.

I. Perhaps most important is the transfer of hydrogen to the oxygen which holds the metal (let M = metal): $H{-}CO{-}OM \rightarrow CO + [MOH]$, which, in the presence of CO_2, gives $M_2CO_3 + H_2O$. This applies to all cases wherein the ratio of carbon monoxide to hydrogen in the gases is greater than 1:1. With lithium formate, for example, the ratio is 10:1. From 10 grams of the salt, 1103 cc. of carbon mon-

[8] Fischer, Tropsch and Schellenberg, ref. 6, p. 355.
[9] Goldschmidt, *Chem. Ztg.* **31**, 608 (1907).
[10] Hofmann and Schibsted, *Ber.* **51**, 1398 (1918).
[11] Hofmann and Schumpelt, *Ber.* **49**, 306 (1916).

oxide, 113 cc. of hydrogen and 15 cc. of methane comprise the gaseous portion. Excessive amounts of carbon monoxide in comparison with hydrogen are observed from formates of the following metals.

Formate	Li	Mg	Ba	Rare-earths	Na	K	UO_2	Ca	Mn	Fe″
Ratio $CO : H_2$	10	5.7	3.2	2-4	3.6	2.7	1.8	1.5	2	1.1

The reverse holds true with formates of the metals listed below.

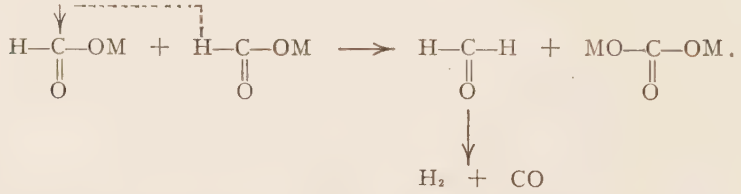
Formate	Ni	Pb	Zn	Cu
Ratio $CO : H_2$	0.38	——	0.18	0.06

II. Hydrogens from two different molecules combine, leaving the oxalate or its product of decomposition. If the oxalate were to decompose entirely into carbonate and carbon monoxide, this would give a maximum carbon monoxide-hydrogen ratio of 1 : 1.

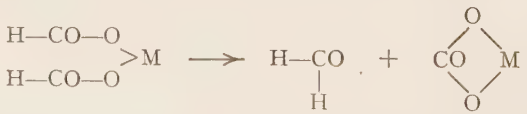
$$2H—CO—OM \longrightarrow H_2 + (CO_2M)_2.$$

This type of pyrolysis is especially encountered with formates of K, Na, Cu, Pb, Ni. In other words, it is encountered with alkali metals of large atomic volumes which form fairly stable oxalates, or with metals whose oxides are fairly strong oxidizing agents towards hydrogen. Thus, metallic residues of copper, lead and nickel are left, following the pyrolysis of their respective formates. Ten grams of nickel formate yields 310 cc. of carbon monoxide, 804 cc. of hydrogen, and 50 cc. of methane.

III. The OM group in one molecule is displaced by the H of another:



Since only one oxygen linking need be disturbed in formates of bivalent or multivalent metals, conceivably they should follow this scheme more readily than when M is univalent.



The carbonate, MCO_3, changes in part into $CO_2 + MO$. Hofmann and Schibsted assert that the carbonate or oxide residue is highly catalytic and that most of the formaldehyde is changed at once

into methyl formate, methanol or formic acid, and that whatever formaldehyde actually appears in the final product is a result of the decomposition of methyl formate. As much as 20 percent of the theoretical quantity of methyl formate is produced from zinc formate at 260-280°. Under the most favorable conditions, zinc formate gives a 25 percent yield of formaldehyde, and a 40 percent yield of reducing substances. Ten grams of the salt produces 184 cc. of carbon monoxide, 1023 cc. of hydrogen, and 15 cc. of methane. Formates of the rare earth metals give considerable quantities of formaldehyde. With formates of strongly basic metals, very little formaldehyde is obtained, possibly because of the higher temperature of the decomposition, and possibly because of the basic character of the residue. From them, the distillate consists chiefly of methanol, acetone, furfural and empyreumatic substances. The more slowly the salt is heated, the more the gaseous products increase at the expense of the acetone and the methanol.

The following data give evidence of the catalytic nature of the zinc oxide residue. Normally, formic acid pyrolyzes only into $H_2 + CO_2$, or into $H_2O + CO$, but when its vapors are passed over zinc oxide, considerable amounts of methanol and formaldehyde result. Thoria behaves similarly. There may be intermediate salt formation in these cases.

The following series shows the metals whose formates give formaldehyde and related substances: $Zn > UO_2 > Th > Er > Yt > Didym > Ce > Mn'' > Cu'' > Fe''$. Aluminum formate gives no formaldehyde or methanol. Regarding the mechanisms I, II and III, lithium formate decomposes 4.5 times more rapidly by I than by II and III. With the formates of the following metals the rate is as follows: Mg, 2.5 times as rapidly; Ba, with equal speed for both; Th, twice as rapidly; Yt, Er, Didym, Ce, 1-0.5 times; Na, K, with equal speed; and UO_2, Ca, at half the rate.

IV. Two formates condense into a basic glyoxylate, caused by the wandering of the hydrogen of one molecule to the carbonyl-oxygen of the other:

This course of pyrolysis leads to the production of furfural and other ring compounds; also to the production of acetone, methanol and empyreumatic substances. It is particularly apparent with lithium, barium, calcium and magnesium formates.

Oxalates. Reference has already been made [12] to the pyrolysis of *sodium oxalate*. There is some decomposition into oxides of carbon (more carbon dioxide than carbon monoxide) at temperatures as low as 160°, but the fact that sodium oxalate is prepared from sodium formate at temperatures of 350-400° is indicative of the slow rate of decomposition at these temperatures. Some free carbon is also formed, possibly from the reaction:

$$2CO \longrightarrow C + CO_2,$$

which tends to catalyze further decomposition. Attempts to force carbon monoxide into interaction with sodium carbonate failed even at 1100 atmospheres pressure. Since this is far in excess of the calculated pressure, this result seems to indicate that the decomposition of sodium oxalate is irreversible.

Herschkowitsch [13] has suggested that the primary decomposition of all oxalates gives carbon dioxide and the metal, but that such readily oxidizible metals as sodium, potassium or calcium reduce half of the carbon dioxide giving thereby the carbonate and carbon monoxide. Less readily oxidizible metals such as iron or lead reduce only a part of the carbon dioxide, and a mixture of metal and metallic oxide is found in the residue. Thus, ferrous oxalate yields a residue which is about half metallic iron and the remainder is ferrous oxide. Lead oxalate gives lead suboxide, Pb_2O. In the case of nickel oxalate, the residue after heating is almost pure metallic nickel, and the gaseous product is mainly carbon dioxide with very little carbon monoxide.

Sodium hydrogen oxalate [14] pyrolyzes into carbon monoxide, carbon dioxide and water at 210°; between 300-350° it yields disodium oxalate, free from sodium carbonate; and at 400° the following products may be identified as carbon dioxide, carbon monoxide, water, formic acid and sodium carbonate. Potassium hydrogen oxalate behaves similarly.

Calcagni lists 400° as the decomposition temperature [15] of calcium oxalate and of barium oxalate. Strontium oxalate gives carbon monoxide and carbon dioxide at 200°, and magnesium oxalate behaves similarly at 290°. A quantitative method [16] for the determination of calcium is based on the thermal decomposition of calcium oxalate in an atmosphere of carbon dioxide. In this manner, calcium carbonate was quantitatively formed in 15 minutes at 675-800°.

Moles and Villamil [17] give 370° as the point at which calcium oxalate

[12] Ott, *Z. physik. Chem.* **109**, 1 (1924); *see* original for many details.
[13] Herschkowitsch, *Z. anorg. allgem. Chem.* **115**, 159 (1921).
[14] Calcagni, *Gazz. chim. ital.* **50**, 1, 245 (1920).
[15] *See also* de Coninck and Raynaud, *Bull. soc. chim.* **9**, 301 (1911).
[16] Foote and Bradley, *J. Am. Chem. Soc.* **48**, 676 (1926).
[17] Moles and Villamil, *Anales soc. espan. fis. quim.* **22**, 174 (1924); **24**, 465 (1926); *Chem. Abstracts* **18**, 2295; **21**, 2594.

starts to decompose into calcium carbonate and carbon monoxide; above 440°, the products of pyrolysis approach the equation:

$$7CaC_2O_4 \longrightarrow 7CaCO_3 + 5CO + CO_2 + C.$$

At 430-440°, calcium oxalate [7] evolves gases which analyze as follows: carbon monoxide 93 percent; carbon dioxide 4 percent; hydrogen 3 percent. The source of the hydrogen is puzzling.

Acetates and Related Salts.

The preparation of ketones by distilling the calcium salts of organic acids is one of the very familiar reactions of organic chemistry. Williamson [18] discovered it:

$$(RCO_2)_2Ca \longrightarrow R_2CO + CaCO_3.$$

Modifications of this procedure lead to the formation of mixed ketones, aldehydes or hydrocarbons. Mixed ketones are formed (Williamson) when a mixture of salts is heated; aldehydes,[19] when the mixture of a salt and calcium formate is heated; and hydrocarbons, when the salt is mixed with hydroxide before heating.

If the pure salt is taken, fairly high yields of good product may be expected if the temperature of the reaction does not exceed the decomposition temperature of the desired ketone. This condition is realized with the simple ketones of low molecular weight. For the ketones of high molecular weight, a vacuum is desirable.

When mixtures are taken (two salts, or salt with hydroxide), mixtures must also be expected in the products of reaction. In many cases, however, it has not been difficult to find a fairly effective means of separation of the desired product. Therefore, this reaction has had wide usage. The following equations represent these cases.

1. $Ca(O—CO—R)_2 + Ca(O—CO—R')_2 \longrightarrow 2CaCO_3 + R—CO—R'.$
   The by-products are R_2CO, and R'_2CO; usually also saturated and unsaturated hydrocarbons, and CO_2, CO, H_2, etc.

2. $Ca(O—CO—R)_2 + Ca(O—CO—H)_2 \longrightarrow 2CaCO_3 + 2R—CHO.$
   The by-products are R_2CO and HCHO, or H_2+CO.

3. $Ca(O—CO—R)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2RH.$
   The by-products are R_2CO, R—R, H_2, etc. Better yields of hydrocarbon result from heating $R—CO_2Na + NaOH$, since sodium salts give poorer yields of ketone (see below).

The distillation of the calcium salt with calcium formate is Krafft's method [19a] for the preparation of higher aliphatic aldehydes. It has been shown that the aldehydes thus produced (stearic and palmitic aldehydes)

[18] Williamson, *Ann.* **81**, 86 (1852); *see also*, Friedel, *Ann.* **108**, 122 (1858); Ludlam, *Chem. Soc.* **81**, 1185 (1902).
[19] Limpricht, *Ann.* **97**, 368 (1856), Piria, *Ann. chim. phys.* [3] **48**, 113 (1856).
[19a] Krafft, *Ber.* **13**, 1413 (1880).

are the dimers, $(RCHO)_2$, of the simple aldehydes, but that depolymerization into RCHO may be effected [19b] by vacuum distillation.

Acetates of the Calcium Type.

Although traces of acetone first make their appearance at 160°, the rate at which acetone is formed [20] is quite low until the temperature rises well above 400°. Temperatures between 430-490° are recommended, but considerable loss ensues unless the acetone vapors are swept away by an inert gas stream (nitrogen or carbon dioxide) as soon as formed. Yields between 90-100 percent may be realized in this manner after 1-2 hours' heating. Ardagh points out that many statements in the literature which advocate temperatures of 400° or less are "clearly wide of the mark".

An interesting phase of catalysis is represented in the continuous process for the conversion of acetic acid into acetone. Various catalysts have been recommended, all operating at about 485-500°. Sabatier [21] mentions calcium carbonate as the catalyst; another modification is the use of magnesium, calcium or barium acetates on pumice; [22] in another process,[23] iron balls are coated with hydrated lime, admixed with a little magnesia. The yields of acetone range between 80-90 percent of the theory. In Sabatier's opinion, the acid vapors are first converted into the salt which, being unstable at the temperature of its formation, undergoes pyrolysis into the ketone, thereby regenerating the "catalyst". Sabatier's viewpoint has been presented on p. 193.

The yield of acetone from various acetates is profoundly influenced by the metallic part of the molecule. Dry distillation of lithium acetate, according to Rojahn and Schulten,[24] leads to a 93 percent yield of acetone, as compared with a 50 percent yield from sodium acetate. Comparative experiments by Krönig [25] gave the following yields of acetone:

Table XLV. *Effect of the Metal on the Yield of Acetone from Metallic Formates.*

Metallic Acetate	Yield of Acetone Percent	Metallic Acetate	Yield of Acetone Percent
Lithium	100	Manganous	66.3
Barium	89	Sodium	37.5
Calcium	82.5	Potassium	11.6
Magnesium	75.9	Lead	87.0

[19b] Feulgen and Behrens, *Z. physiol. Chem.* **177**, 221 (1928).
[20] Ardagh and others, *Ind. Eng. Chem.* **16**, 1133 (1924).
[21] Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co. **1922**, paragraphs 161 and 829.
[22] Kekre, Sudborough and Watson, *J. and Proc. Asiatic Soc. Bengal* **18**, 6 (*Proc. 9th Indian Sci. Congress* lxxvii (1922); *Chem. Abstracts* **18**, 1468 (1924).
[23] Rooney, *Chem. Met. Eng.* **22**, 847 (1920).
[24] Rojahn and Schulten, *Ber.* **59**, 499 (1926).
[25] Krönig, *Z. angew. Chem.* **37**, 667 (1924).

Better yields from barium acetate than from calcium acetate are reported also in reference 22.

Lead acetate also yields metallic lead. This is indicative of the fact that part of the acetone was oxidized in the process:

$$8Pb(O{-}CO{-}CH_3)_2 \longrightarrow 7CH_3COCH_3 + 8Pb + 11CO_2 + 3H_2O.$$

The lead salt of hydracrylic acid appears to behave differently, for it yields [26] acrylic acid when heated between 150-200°.

It has long been known [27] that distillation of *barium propionate* gives diethyl ketone. Higher methyl ketones, $R{-}CO{-}CH_3$, ($R = C_{10}H_{21}{-}$ to $C_{19}H_{39}{-}$) are prepared [28] by distillation under diminished pressure of a mixture of the required barium salt with three mols of barium acetate. The superiority of barium salts has been mentioned above. As would be expected, methyl heptadecyl ketone, $C_{17}H_{35}COCH_3$, is formed [29] when barium stearate and barium acetate are heated together. Quite similarly,[30] distillation of a mixture of calcium formate and calcium geranate $[(CH_3)_2C{=}CH{-}CH_2CH_2C(CH_3){=}CH{-}CO_2]_2Ca$ yields citral. Phenyl acetaldehyde may be synthesized [31] in like fashion from a mixture of calcium phenylacetate and calcium formate, whereas acetophenone may be prepared by heating a mixture [32] of calcium benzoate and calcium acetate.

Magnesium salts of organic acids [32a] appear to give about the same yields of products at similar temperatures as do the salts which are formed by the addition of carbon dioxide to Grignard reagents. For this reason, Ivanov suggests that the older structure, RCO_2MgX, is less suitable than the one proposed by Jolibois, namely, $(RCO_2)_2Mg.MgX_2$. At 330-360°, the acetate pyrolyzes into acetone in 57 percent yield, and the propionate similarly gives diethyl ketone in 70 percent yield. The yields of ketones are poor with Grignard reagents formed from aryl, hydroaryl or secondary alkyl halides. Thus, the benzoate, at 460-500°, changes into benzophenone in 6 percent yield. Chiefly, the reaction products in these cases are hydrocarbons.

Acetates of Silver, Copper and Mercury.

These cases differ from the other acetates that have been mentioned in that acetic acid, and not acetone, comprises the distillate. From 8.2

[26] Beilstein, *Ann.* **122**, 372 (1862).
[27] Morley, *Ann.* **78**, 187 (1851).
[28] Morgan and Holmes, *J. Soc. Chem. Ind.* **44**, 108T (1925).
[29] Krafft, *Ber.* **12**, 1672 (1879).
[30] Tiemann, *Ber.* **31**, 827 and 2899 (1898).
[31] Cannizzaro, *Ann.* **119**, 254 (1861).
[32] Friedel, *Compt. rend.* **45**, 1014 (1857).
[32a] Ivanov, *Bull. soc. chim.* **43**, 441 (1928).

grams of silver acetate, Iwig and Hecht [33] identified 2.1 grams of acetic acid (acetone free), 5.3 grams of silver, 0.56 gram of carbon dioxide and 0.13 gram of carbon. The reaction started at 210° and was complete at 240°. The equation to represent these facts is:

$$4CH_3CO_2Ag \longrightarrow 3CH_3CO_2H + 4Ag + CO_2 + C.$$

A general equation:

$$2n\ R{-}CO_2Ag \longrightarrow (2n-1)\ R{-}CO_2H + 2n\ Ag + (n-1)\ C + CO_2,$$

suggested by these investigators, appears to be satisfactory in the case of the pyrolysis of *silver n-butyrate*. This compound decomposes less smoothly than the acetate, but in the decomposition product from 15 grams there was identified 5.9 grams of butyric acid, 8.3 grams of silver, 0.73 gram of carbon and 0.42 gram of carbon dioxide. In this case, therefore, there is evidence for the equation:

$$8C_4H_9{-}CO_2Ag \longrightarrow 7C_4H_9{-}CO_2H + 8Ag + 3C + CO_2.$$

Kachler [34] reported nearly a quantitative agreement with the general equation when working with silver acetate, *iso*valerate, *n*-caproate and heptoate, and a fair agreement with the palmitate, lactate, benzoate, phenylacetate and hydroxy*iso*butyrate. Reference will be made later (p. 497) to the pyrolysis of other silver salts. There it will be shown that the $-CO_2Ag$ group may not only be replaced by $-CO_2H$, but also by $-H$; in other words, decarboxylation of acids may frequently be effected by heating the silver salts.

Cupric acetate [25] and mercurous acetate are similar in that they both yield acetic acid and free metal on distillation. The cupric salt appears to pyrolyze in accordance with the equation:

$$2Cu(O{-}CO{-}CH_3)_2 \longrightarrow 3CH_3CO_2H + 2Cu + CO_2 + C.$$

Mercurous acetate [35] starts to decompose at 270° (bath temperature), and vigorous gas evolution ensues until about 400°. Mercury, acetic acid, carbon and carbon dioxide are important products of the reaction. Possibly the equation for their formation is:

$$2Hg_2(O{-}CO{-}CH_3)_2 \longrightarrow 3CH_3CO_2H + 4Hg + CO_2 + C,$$

although this equation alone would furnish a very incomplete picture of the experimental results. Carbon monoxide and methylmercuric acetate, $CH_3{-}Hg{-}O{-}CO{-}CH_3$, are also definite products of the reaction. Possibly the carbon monoxide results in part from the interaction of carbon and carbon dioxide. In one experiment, which was

[33] Iwig and Hecht, *Ber.* **19**, 238 (1886).
[34] Kachler, *Monatsh.* **12**, 338 (1891).
[35] Hurd, unpublished results.

performed in a carbon dioxide atmosphere, 32 grams of mercurous acetate was found to yield 312 cc. of alkali-insoluble gas, that contained 95-96 percent carbon monoxide. Usually, about one mol of carbon monoxide appears for each 4.5-5 mols of mercurous acetate taken.

During the distillation of mercurous acetate, sublimation crystals of methylmercuric acetate (melting point 128°) accumulate in the cooler parts of the apparatus. This has also been observed [36] by Sneed and Maynard, who heated mercurous acetate in an atmosphere of nitrogen. The mechanism for its production may involve merely the elimination of carbon dioxide and mercury:

$$CH_3—CO—O—Hg—Hg—O—CO—CH_3 \longrightarrow Hg + CO_2 + CH_3—Hg—O—CO—CH_3.$$

Professor Sneed suggests that mercur*ous* dimethyl may appear as a non-isolable intermediate step:

$$Hg_2(OCOCH_3)_2 \longrightarrow 2CO_2 + [CH_3—Hg—Hg—CH_3] \longrightarrow Hg + Hg(CH_3)_2.$$

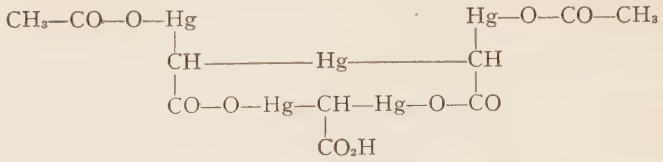
As indicated, this would decompose into mercury and dimethyl mercury. Then the latter would react with unused mercurous acetate:

$$Hg_2(OCOCH_3)_2 + Hg(CH_3)_2 \longrightarrow 2CH_3Hg—O—CO—CH_3 + Hg.$$

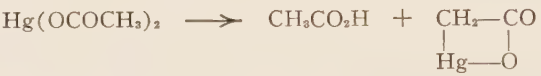
In support of this mechanism, it may be stated that the carbon-to-mercury linkage is frequently established, by loss of carbon dioxide, when certain mercury salts are heated; these will be presented shortly. It is also pertinent to note that the radical, CH_3Hg, has been obtained [37] as a cathodic deposit at liquid ammonia temperatures; at room temperature, this disproportionates into mercury and dimethyl mercury.

Mercuric acetate, at 170-180°, becomes transformed into a well defined compound, which was described, but not analyzed or named, by F. Stromeyer in 1809. This substance dissolves completely in sodium hydroxide solution without any separation of mercuric oxide. It is, therefore, a true metallo-organic compound, and probably it was the first metallo-organic compound to be discovered. Gmelin mentioned it in his "Handbuch". Recently, this substance has been found [38] to possess the formula $C_{10}H_{10}O_{10}Hg_5$, and has been named "mercuretin". The same compound gradually separates if mercuric acetate is heated in acetic acid, and it is formed completely and at once on the addition of acetic anhydride to such a solution. The structural formula assigned to mercuretin is:

[36] Sneed, University of Minnesota, private communication, 1927.
[37] Kraus, *J. Am. Chem. Soc.* **35**, 1740 (1913).
[38] Marsh, Fleming and Struthers, *J. Chem. Soc.* **1927**, 2658.



Dimroth [39] had previously recognized the production of a mercurated acetic acid, or an anhydride of such a substance. The equation for its formation:



is obviously in error on the basis of the work of Marsh, Fleming and Struthers. If mercuric acetate is heated in a sealed tube at 190°, no mercurous acetate is formed simultaneously, nor is there any permanent gas.

Salts of Higher Organic Acids.

Calcium butyrate has assumed recent interest, because dipropyl ketone, formed from it by pyrolysis [40] at 300-400°, may prove to be of importance as a motor fuel. Desiccated sand or clay serves as a diluent during the heating. "Ketol" is a name given to this motor fuel, boiling point 60-200°, which is composed chiefly of butyrone [41] but which also contains other ketones.

Two kg. of calcium isobutyrate gives [42] about 700 grams of distillate, 110 grams of which is an aqueous lower layer. The upper layer of distillate is composed of *iso*butyraldehyde, methyl *iso*propyl ketone, di*iso*propyl ketone, and certain unidentified substances. Less than one-third of the total distillate is di*iso*propyl ketone. Likewise, *calcium isovalerate* gives a rather complex thermal decomposition. The pyrolysis [43] starts at 400° and continues to 600°. From 900 grams of the salt, Dilthey isolated 287 grams of a ketone-aldehyde mixture, 323 grams of olefine bromides, and about 45 liters of gas. By volume, the gas analyzed as follows; methane 32.97 percent, hydrogen 23.4 percent, carbon monoxide 23.0 percent, and ethane 20.61 percent. The olefines were chiefly butylenes, accompanied, however, by ethylene, propylene and traces of higher olefines. Valerone, valeraldehyde, methyl *iso*butyl

[39] Dimroth, *Ber.* **35**, 2870 (1902); Whitmore, "Organic Compounds of Mercury," New York, The Chemical Catalog Co., **1921**, p. 141.
[40] Lefranc, Can. Pat. 257,435, Jan. 19, 1926; Brit. Pat. 216,120, May 17, 1923. *Chem. Abstracts* **19**, 77; **20**, 2332. U. S. Pat. 1,656 488; *Chem. Abstracts* **22**, 965 (1928).
[41] Dépasse, *Bull. Assoc. chim. sucr. dist.* **43**, 409 (1926); *Chem. Abstracts* **21**, 296 (1927)
[42] Barbaglia and Gucci, *Ber.* **13**, 1572 (1880); Glückmann, *Monatsh.* **16**, 897 (1905).
[43] Dilthey, *Ber.* **34**, 2115 (1901).

ketone and fairly large amounts of other higher ketones were identified in the aldehyde-ketone mixture.

Dibenzyl ketone [44] is formed when calcium phenylacetate is pyrolyzed. If the barium salt [45] is employed, a 50 percent yield is obtained by distilling at 200 mm. Pyrolysis of calcium hydrocinnamate [46] in a current of carbon dioxide [47] produces dibenzyl acetone, $(C_6H_5CH_2CH_2)_2CO$.

Barium diphenylacetate, $Ba(O—CO—CH(C_6H_5)_2)_2$, is of more than ordinary interest because it produces [48] some tetraphenylallene, $(C_6H_5)_2C=C=C(C_6H_5)_2$, during its dry distillation. Originally, Vorländer considered the allene to be a pyrolytic product of tetraphenylacetone, $(C_6H_5)_2CH—CO—CH(C_6H_5)_2$, but this could not be confirmed [49] by his later work (see p. 257), since no tetraphenylallene was isolable from tetraphenylacetone after the latter was passed through a 10 cm. red-hot tube. In fact, there is no case on record wherein an allene is formed from a ketone by thermal dehydration. The source of the allene in the present case is still a matter of conjecture.

In an endeavor to induce a similar type of pyrolysis, Singh [50] heated barium *p*-dimethylaminodiphenylacetate, $\left(\begin{matrix}(CH_3)_2N—C_6H_4\\ \\ C_6H_5\end{matrix}>CH—CO_2\right)_2Ba$ in a high vacuum without obtaining any allene. Instead, the ketone, $\left(\begin{matrix}(CH_3)_2N—C_6H_4\\ \\ C_6H_5\end{matrix}>CH—\right)_2CO$ and *p*-benzyldimethylaniline, $(CH_3)_2NC_6H_4—CH_2C_6H_5$, were isolated.

Soaps.

Distillation [51] of sodium stearate at 13-15 mm. yields paraffins, the most abundant of which are reported to be $C_{10}H_{22}$, $C_{14}H_{30}$, $C_{15}H_{32}$ and $C_{34}H_{70}$. Grün and Wirth, on the other hand, observed [52] no resultant high molecular weight paraffins at a temperature of 550-600° and a pressure of 12-15 mm. From 100 grams of sodium stearate there was produced 55-62 grams of an unsaturated distillate, melting point 50.5-54.8°. About 1 gram of 17-pentatriacontanone was also found.

Sodium oleate (Pictet and Potok) distils chiefly to olefines such as C_9H_{18}, $C_{10}H_{20}$, $C_{11}H_{22}$ and $C_{13}H_{26}$. Apparently, naphthenes are not

[44] Popow, *Ber.* **6**, 560 (1873).
[45] Stobbe, Russwurm and Schulz, *Ann.* **308**, 175 footnote (1899).
[46] Dunschmann and von Pechmann, *Ann.* **261**, 188 (1890).
[47] Manchot and Krische, *Ann.* **337**, 188 (1904).
[48] Vorländer and Siebert, *Ber.* **39**, 1024 (1906).
[49] Vorländer and Rack, *Ber.* **56**, 1125 (1923).
[50] Singh, *J. Chem. Soc.* **127**, 2445 (1925).
[51] Pictet and Potok, *Helv. Chim. Acta* **2**, 501 (1919).
[52] Grün and Wirth, *Ber.* **53**, 1301 (1920).

formed. From 1 kg. of sodium soaps, prepared from herring oil,[53] the following data were recorded: 171 grams of water; 528 grams of an oil; 73.5 liters of gas, particularly methane; 184 grams of residue (61 percent sodium carbonate, 2.5 percent sodium oxide, 3.1 percent sodium chloride, and 31.6 percent insoluble).

Distillation of barium palmitate [54] yields palmitone, and distillation of calcium stearate,[55] stearone. Similarly, calcium myristate yields myristone,[56] and barium laurate, laurone. Laurone is best prepared [57] by mixing barium laurate with soda-lime, and then distilling in a vacuum of 15 mm. Recent work with calcium stearate [58] indicates that it begins to undergo pyrolysis at 400°, and that at 500° the distillate is soluble in acetone to the extent of 38 percent. Stearone may be isolated from either calcium or magnesium stearates (450-480° and 5-7 mm.), and oleone from the corresponding oleates. Magnesium stearate starts to decompose at 300° and at 400° the acetone-soluble material represents 80 percent of the distillate.

It seems that the best results for a fuel oil from the calcium or magnesium soaps from soya-bean oil are obtained by heating the soap several hours below 450°, and then distilling above 500°. The material from the magnesium soap distils more rapidly.

Salts of Hydroxy Acids.

The formation of acrylic acid from lead hydracrylate has already been mentioned. Calcium lactate,[59] if heated gently to 180°, forms dilactic acid, $O(CHCH_3—CO_2H)_2$. It will be recalled that this acid yields an acid anhydride even by vacuum distillation (p. 416). Calcium ethoxyacetate [60] behaves normally, in that it gives rise to symmetrical diethoxyacetone:

$$(C_2H_5O—CH_2—CO_2)_2Ca \longrightarrow CaCO_3 + (C_2H_5O—CH_2)_2CO.$$

Water and alcohol are also in the distillate.

Barium ricinoleate,[61] $(C_6H_{13}—CHOH—CH_2—CH=CH—(CH_2)_7—CO_2)_2Ba$, behaves singularly when it is distilled in a vacuum. It leaves a residue of the isomeric barium ricinate, and yields methylhexyl ketone as distillate. (See p. 479 for the pyrolysis of metallic glyoxalates.)

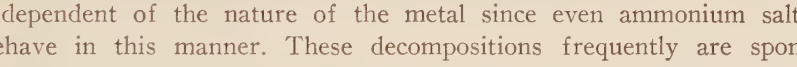
[53] Hirose and Yamada, *J. Chem. Ind.* (Japan) **25**, 1428 (1922); *Chem. Abstracts* **17**, 2059.
[54] Piria, *Ann.* **82**, 249 (1852).
[55] Heintz, *Jahresber.* **1855**, 515.
[56] Overbeck, *Ann.* **84**, 290 (1853).
[57] Krafft, *Ber.* **15**, 1712 (1882).
[58] Sato, *J. Soc. Chem. Ind.* (Japan) **30**, 242-260 (1927); *Chem. Abstracts* **21**, 2371.
[59] Tanatar and Tschelebijew, *Ber.* **23** Ref., 325 (1890).
[60] Gintl, *Monatsh.* **15**, 803 (1895).
[61] Krafft, *Ber.* **21**, 2736 (1888).

Salts of Halogen Substituted Acids.

A general reaction of the sodium salts of **α-bromo acids** is the formation of lactides when they are heated:

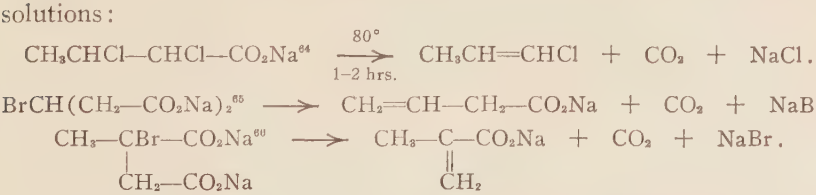
In the case of sodium α-bromopropionate,[62] lactide (and no acrylic acid) is formed by vacuum distillation. The decomposition temperature is about 250-255°. Sodium α-bromobutyrate, by vacuum distillation, gives a small amount of crotonic acid but chiefly gives the anticipated homolog of lactide. The sweet taste of this homolog is in contrast to lactide. With sodium α-bromo*iso*butyrate, the chief vacuum-distillation product is methacrylic acid, and there is almost none of the lactide. About a 10 percent yield of α-hydroxy*iso*butyric acid is also formed.

An unsaturated compound is formed when **β-halogenated salts** are heated. Carbon dioxide is eliminated, and this effect appears to be rather independent of the nature of the metal since even ammonium salts behave in this manner. These decompositions frequently are spontaneous. Rarely does the temperature need to exceed 100°. Therefore, the decomposition is usually effected by heating an aqueous solution of the salt. For example, a warm solution of the sodium salt of α-methyl-β-iodobutyric acid decomposes readily [63] into butene-2:



Apparently the nature of the olefine which is formed in this reaction depends on the method of preparation of the original salt. If prepared from tiglic acid (with HI), the butene boils at 1-1.5°, whereas if prepared from angelic acid the boiling point is 2-2.7°. The two unsaturated hydrocarbons are, therefore, considered to be stereoisomers.

The following equations represent reactions, all of which occur in hot solutions:



[62] Bischoff and Walden, *Ber.* **26**, 263 (1893); *Ann.* **279**, 71, 100 (1894); Bischoff, *Ann.* **279**, 162 (1894).
[63] Pagenstecher, *Ann.* **195**, 115 (1879); Wislicenus, Talbot and Henze, *Ann.* **313**, 239 (1900).
[64] Wislicenus, *Ann.* **248**, 297 (1888).
[65] Wislicenus, *Ber.* **32**, 2047 (1899).
[66] Fittig, *Ann.* **188**, 81 (1877).

These cases indicate the comparative stability of the $—CO_2Na$ group in the α-position.

Unsaturated compounds, which possess a β-halogen atom, should be capable of decomposition into members of the acetylene series. In accordance with this, it has been found [67] that sodium dichloroacrylate, $Cl_2C{=}CH{—}CO_2Na$, decomposes spontaneously into chloroacetylene, $ClC{\equiv}CH$. Furthermore, it might be argued that geometric isomers of this type, $\begin{matrix} R{—}C{—}Br \\ \| \\ R{—}C{—}CO_2Na \end{matrix}$ and $\begin{matrix} Br{—}C{—}R \\ \| \\ R{—}C{—}CO_2Na \end{matrix}$, would reveal differences in stability. This is borne out by experience. It has been customary to regard the former, the *cis* isomer, as the compound which should decompose the easier. Thus, the potassium salt of β-bromoangelic acid, $\begin{matrix} CH_3{—}C{—}Br \\ \| \\ CH_3{—}C{—}CO_2K \end{matrix}$, is smoothly transformed [68] in hot water into dimethyl acetylene, whereas the salt from the isomeric β-bromotiglic acid is not appreciably changed at 100°. Similarly, silver β-chloro*iso*crotonate, $\begin{matrix} CH_3{—}C{—}Cl \\ \| \\ H{—}C{—}CO_2Ag \end{matrix}$, changes into methyl acetylene more easily than silver β-chlorocrotonate.

The decomposition [69] of the ammonium salt of *dl*-β-phenyl-β-bromopropionic acid is noticeable at room temperature, and is rapid at 60°:

$$C_6H_5CHBr{—}CH_2{—}CO_2NH_4 \longrightarrow C_6H_5CH{=}CH_2 + CO_2 + NH_4Br.$$

The diethylammonium salt is still less stable. It decomposes rapidly at 45°. Cinnamic acid is also a product of these decompositions.

Krafft [70] has described an interesting synthesis of dehydroundecylenic acid which consists in the vacuum distillation (12 mm.) of potassium monobromoundecylenate at 250°:

$$CHBr{=}CH{—}(CH_2)_8{—}CO_2K \longrightarrow KBr + CH{\equiv}C{—}(CH_2)_8{—}CO_2H.$$

Salts of Amino Acids and Related Compounds.

At 180-185°, calcium acid glutamate is decomposed [71] into calcium pyrrolidone-carboxylate:

$$(HO_2C{—}CH_2CH_2{—}CHNH_2{—}CO_2)_2Ca \longrightarrow \left(\begin{matrix} CH_2{—}CH_2 \\ | \quad | \\ CO \quad CH{—}CO_2 \\ \diagdown \diagup \\ NH \end{matrix}\right)_2 Ca + H_2O$$

[67] Wallach, *Ann.* **203**, 88 (1880).
[68] Wislicenus and Henze, *Ann.* **313**, 243 (1900).
[69] Senter and Ward, *J. Chem. Soc.* **127**, 1847 (1925).
[70] Krafft, *Ber.* **29**, 2234 (1896).
[71] Abderhalden and Kautzsch, *Z. physiol. Chem.* **64**, 448 (1910).

In other words, this is in reality the decomposition of a γ-amino acid instead of a calcium salt. In general, the literature dealing with the pyrolysis of salts of amino acids is lacking.

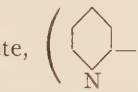
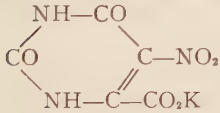
Investigation [72] of the magnesium salt of phenylcarbamic acid has revealed that it changes into symmetrical diphenyl urea at 250-270°:

$$(C_6H_5NH{-}CO{-}O)_2Mg \longrightarrow (C_6H_5NH)_2CO + CO_2 + MgO.$$

It would be interesting to learn if the course of the reaction progressed through a preliminary dissociation into phenyl *iso*cyanate, since this is fairly customary for carbamic derivatives.

When calcium anilinoacetate,[73] $(C_6H_5NH{-}CH_2{-}CO_2)_2Ca$, is subjected to glowing temperatures, traces of indole are formed. When it is heated with calcium formate, the yield of indole is increased to 5.3 percent. The following equation is given to represent this change:

$$(C_8H_8NO_2)_2Ca + (HCO_2)_2Ca \longrightarrow CaCO_3 + 2H_2O + 2C_8H_7N.$$

α,α-Bipyridyl may be formed [74] in about 17 percent yield through the pyrolysis of cupric picolinate,  . Carbon dioxide is evolved from the potassium salt [75] of 5-nitrouracil-carboxylic acid-(6),  , at 130°, as it is converted into the potassium salt of nitrouracil.

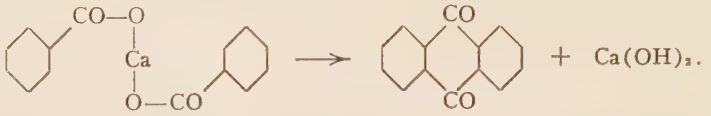
Salts of Aromatic Acids.

It will be recalled that acetone was formed in particularly high yields during the pyrolysis of lithium acetate (p. 482). Lithium benzoate, on the other hand, yields [76] but 50 percent of benzophenone; and sodium benzoate but 28.2 percent. Calcium benzoate has long been known [77] to give rise to benzophenone on dry distillation, but anthraquinone [78] is also formed as an end product. Thus, there is evidence not only for the equation:

$$(C_6H_5{-}CO_2)_2Ca \longrightarrow (C_6H_5)_2CO + CaCO_3,$$

[72] Terentieff, *Bull. soc. chim.* **35**, 1164 (1924).
[73] Mauthner and Suida, *Monatsh.* **10**, 250 (1889).
[74] Blau, *Monatsh.* **10**, 376 (1889).
[75] Behrend, *Ann.* **229**, 35 (1885); **240**, 5 (1887).
[76] Rojahn and Schulten, *Ber.* **59**, 499 (1926).
[77] Peligot, *Ann.* **12**, 41 (1834). *Chancel, Ann.* **72**, 279 (1849); *Compt. rend.* **28**, 84 (1849).
[78] Kekule and Franchimont, *Ber.* **5**, 909 (1872).

but also for



It is possible to pyrolyze calcium benzoate at a temperature of 420° and 1 mm. pressure instead of 550° and 760 mm. Dosios and Leucaditis [79] favor the mechanism from the salt to the ketone through the acid anhydride:

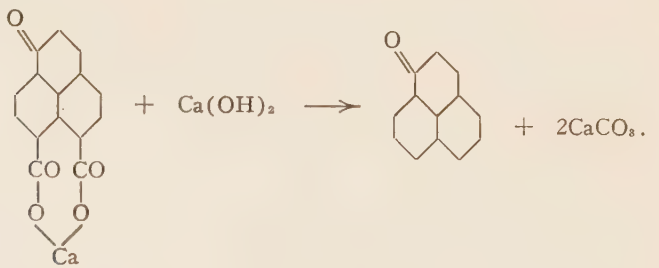
$$(RCO_2)_2Ca \longrightarrow (RCO)_2O + CaO,$$

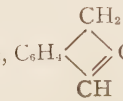
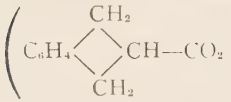
since some acid (as well as ketone) is formed in the distillation of both calcium acetate and calcium benzoate.

This method of preparation of aromatic ketones is rarely used in practice. The vast majority of aromatic ketones are unsymmetrical; therefore, in most cases this method cannot compete with a method such as Friedel and Crafts'. It has been used in a few cases, however.

2,4,2′,4′-Tetramethylbenzophenone results [80] from the dry distillation of calcium 2,4-dimethyl-benzoate.

Bamberger and Philip [81] heated pyrenic acid with an excess of lime, obtaining thereby "pyrene ketone" together with small amounts of naphthalene. As one would expect, the excess of calcium hydroxide induced decarboxylation:

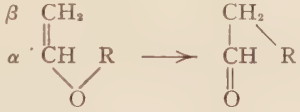


A synthetical method for indene,  , depends on the pyrolysis [82] of the barium salt of hydrindene carboxylic acid,  , at 100 mm. The yield of indene is about 7 grams

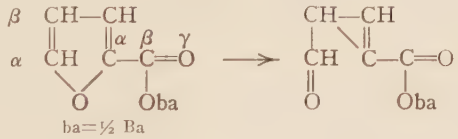
[79] Dosios and Leucaditis, *Compt. rend.* **184**, 1458 (1927).
[80] Boeseken, *Rec. trav. chim.* **26**, 286 (1907).
[81] Bamberger and Philip, *Ann.* **240**, 178 (1887); for structure, *see* Goldschmiedt, *Ann.* **351**, 230 (1907).
[82] Perkin, Jr. and Révay, *J. Chem. Soc.* **65**, 247 (1894).

from 28 grams of the original salt. Neither hydrindene nor the ketone related to it could be isolated as reaction products. Another apparent decarboxylation occurs in the thermal decomposition[83] of barium furoate, $(C_4H_3O—CO_2)_2Ba$. This decomposition commences at 220°, and becomes very rapid at 300°. It is hastened by diminishing the pressure, and the decomposition does not occur if the salt is heated in a sealed tube, even at 350°. About two-thirds of the decomposition product is furan, and the remainder cyclopropene,[84] . Far better than this for the preparation of furan is the pyrolysis of furoic acid, which has already been described.

It is not simple to provide a mechanism to provide for cyclopropene from barium furoate. Freundler, who discovered the reaction, suggested none. The following mechanism provides an explanation for the formation of the cyclopropene nucleus, although as yet it is supported only by analogy to some of the material which was presented under ethers (pp. 203, 206). Barium furoate may be regarded as an ether with α,β and β,γ unsaturation. Just as certain vinyl ethers rearrange when heated:

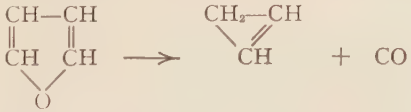


so also barium furoate may possibly undergo a similar rearrangement:



ba=½ Ba

However, since furan itself is reported[84a] to break down at 490° into an unsaturated compound, C_3H_4, which is probably cyclopropene, it is reasonable to infer that there should be no essential difference in accounting for the substance regardless of its origin from furan or from barium furoate. The change from furan to cyclopropene suggests that carbon monoxide is the other product.

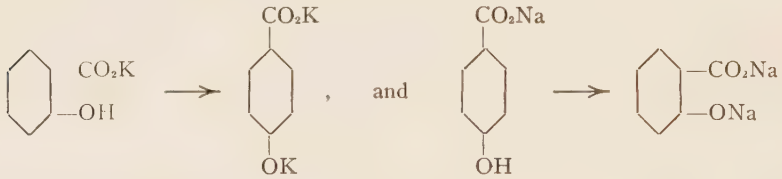


[83] Freundler, *Compt. rend.* **124**, 1157 (1897); *Bull. soc. chim.* [3] **17**, 613 (1897).
[84] For the confirmation of the structure of cyclopropene, *see* Demjanov and Dojarenko, *Ber.* **56**, 2200 (1923).
[84a] Sinkinson, *Ind. Eng. Chem.* **17**, 31 (1925).

A study of the pyrolysis of the alkali salts of salicylic acid leads to a more intelligent interpretation of the Kolbe synthesis. It is known, for example, that carbon dioxide must react with *sodium* phenylate if the salicylate is to be prepared. Under similar circumstances, *potassium* phenylate yields the *para* isomer. Pure sodium salicylate gives none of the *para* isomer if heated as high as 300°, but potassium (or rubidium) salicylate [85] is completely changed into dipotassium (or rubidium) *p*-hydroxybenzoate at 210-220°. On the other hand, neutral sodium *p*-hydroxybenzoate gives high yields [86] of disodium salicylate at 290°. Both of these reactions may be represented by the equation:

$$2C_6H_4\begin{matrix}CO_2K(Na)\\OH\end{matrix} \longrightarrow C_6H_4\begin{matrix}CO_2K(Na)\\OK(Na)\end{matrix} + C_6H_5OH + CO_2.$$

More specifically,

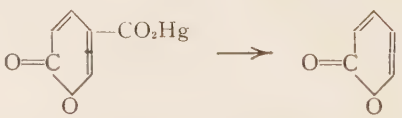


Dry distillation [87] of calcium *o*-phenoxybenzoate, $(C_6H_5O—C_6H_4—CO_2)_2Ca$, leads to the formation of phenol, diphenyl ether and xanthone.

Mercury Salts.

Mercurous acetate and mercuric acetate have already been mentioned (p. 485). The former gives acetic acid, mercury, carbon, oxides of carbon, and methylmercuric acetate. The latter gives mercuretin.

Dry distillation of the mercurous salt of cumalinic acid [88] in a hydrogen stream gives a 30 percent yield of cumalin if care is taken:

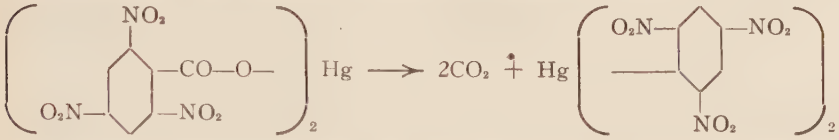


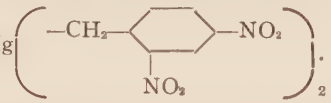
Von Pechmann stated that usually only about half of this quantity of cumalin was isolable.

At the decomposition temperatures, mercuric salts of nearly all organic acids evolve carbon dioxide. In some cases, this becomes a

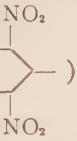
[85] Kolbe *J. prakt. Chem.* [2] **11**, 24 (1875); Velden, *ibid.* **15**, 154 (1877).
[86] Kupferberg, *ibid.* **16**, 425 (1877). Davies, *Z. physik. Chem.* **134**, 57 (1928); Baur, *ibid.* **134**, 87 (1928).
[87] Jeiteles, *Monatsh.* **17**, 66 (1896).
[88] von Pechmann, *Ann.* **264**, 304 (1891).

convenient method for linking mercury to carbon, and this has been developed particularly in the aromatic series. To illustrate: mercuric 2,4,6-trinitrobenzoate [89] yields carbon dioxide quantitatively at 210°, and the product of the reaction is hexanitro-mercury-diphenyl:



In the same quantitative way, the mercuric salt of 2,4-dinitro-phenyl-acetic acid undergoes pyrolysis into carbon dioxide and 2,2′,4,4′-tetranitro-mercury-dibenzyl,  .

The related ethylmercuric salt of trinitrobenzoic acid [90] decomposes at its melting point, 164°, to form a new carbon-to-mercury bond:

(let Ar = ):

$$Ar—CO_2—Hg—C_2H_5 \longrightarrow CO_2 + Ar—Hg—C_2H_5.$$

The phenylmercuric salt, $Ar—CO_2—Hg—C_6H_5$, pyrolyzes similarly [91] in a vacuum at 222°, a temperature 6° below the melting point. The tolyl analog, $Ar—CO_2—Hg—C_6H_4CH_3$, also yields the mixed mercury diaryl, $Ar—Hg—C_6H_4CH_3$, on heating. These cases would lead one to suspect a general behavior, but the methylmercuric salt provides a note of individuality. In a vacuum at 160° (melting point 165°), mercury dimethyl and mercury di-trinitrophenyl are formed:

$$2Ar—CO—O—Hg—CH_3 \longrightarrow 2CO_2 + Hg(CH_3)_2 + HgAr_2.$$

Trinitrobenzoic acid is a compound which loses its carbon dioxide easily when heated (p. 345). This seems to be a rather essential analogy for this type of pyrolysis. It is also encountered in mercuric salts of β-ketonic acids, the instability of which is universally recognized. Mercuric α,α-diethyl-acetoacetate changes quantitatively *in vacuo* at 85° into mercury-*bis*-acetodiethylmethane:

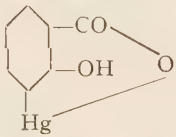
$$(CH_3CO—CEt_2—CO_2)_2Hg \longrightarrow 2CO_2 + (CH_3CO—CEt_2—)_2Hg.$$

The α,α-dimethyl homolog also decomposes quantitatively [92] at 90° in this manner.

[89] Kharasch, *J. Am. Chem. Soc.* **43**, 2238 (1921).
[90] Koten and Adams, *J. Am. Chem. Soc.* **46**, 2764 (1924).
[91] Kharasch and Grafflin, *J. Am. Chem. Soc.* **47**, 1951 (1925).
[92] Kharasch and Staveley, *J. Am. Chem. Soc.* **45**, 2969 (1923).

In the case of aromatic carboxylic acids which do not lose carbon dioxide readily, the mercury usually becomes attached to a carbon of the nucleus. Dimroth [93] has shown that when mercuric benzoate is heated at 170°, the mercury enters *ortho* to the carboxyl group:

$$(C_6H_5CO{-}O{-})_2Hg \longrightarrow C_6H_5CO_2H + \text{C}_6\text{H}_4(\text{CO})(\text{Hg})\text{O}.$$

With mercuric salicylate at 120°, the mercury becomes attached to the carbon which is *ortho* to the hydroxyl group, the formula of the compound being  . In like manner, when the mercury salt of anisic acid [89] is heated, the mercury enters *ortho* to the methoxy group, as it also does with the mercury salt of 3-nitro-4-methoxy-(or hydroxy)-benzoic acid.

Relatively few *mercuric salts of aliphatic acids* have been studied. Mercuric acetate has already received mention. In the pyrolysis of the mercuric salt [94] of phenylacetic acid (above its melting point), or of diphenylacetic acid, the mercury replaces an aromatic hydrogen, thereby indicating that the velocity of mercuration of the nucleus is much greater than that of the side-chain. With mercuric triphenylacetate, $((C_6H_5)_3C{-}CO_2)_2Hg$, there is a more complicated decomposition, but one of the products of the reaction is a nucleus-mercurated-triphenylacetic acid. A peculiar modification is the decomposition in pyridine solution into triphenylmethyl and metallic mercury.

The mercuric salt of trichloroacetic acid is not isolable [94] from aqueous solutions. Invariably, there is a simultaneous oxidation and reduction. Mercurous chloride precipitates whereas carbon dioxide passes from the solution. Neither is mercuric benzoylacetate isolable. Depending on the solvent used for its preparation, its decomposition may be made to proceed in two directions:

In hot alcohol:

$$(C_6H_5CO{-}CH_2{-}CO_2)_2Hg \longrightarrow 2CO_2 + (C_6H_5CO{-}CH_2{-})_2Hg$$

In hot chloroform:

$$(C_6H_5CO{-}CH_2{-}CO_2)_2Hg \longrightarrow C_6H_5CO{-}\underset{\displaystyle Hg{-}O}{\overset{|}{\underset{|}{CH}}}{-}CO + C_6H_5COCH_2CO_2H$$

[93] Dimroth, *Ber.* **35**, 2870 (1902).
[94] Kharasch and Staveley, *J. Am. Chem. Soc.* **45**, 2963 (1923).

In view of the recent work on mercuric acetate (p. 485), it would seem that the *"anhydro-α-hydroxy-mercuribenzoyl acetic acid"* which is formed in hot chloroform is not the simple $C_9H_6O_3Hg$, but a multiple of it such as $(C_9H_6O_3Hg)_5$.

Kharasch has also studied the mode of decomposition of the mercuric salt of phthalide carboxylic acid and of phenylglyoxylic acid. The former melts with decomposition at 195°, and from 1 gram of the salt, 0.36 gram of dihydrophthalide was isolated:

$$\left(C_6H_4{<}\begin{matrix}CH{-}CO{-}O{-}\\ CO\end{matrix}{>}O\right)_2Hg \longrightarrow Hg + 2CO_2 + CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}CH{-}CH{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}CO.$$

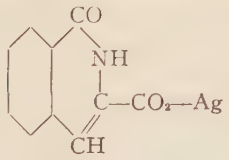
Mercuric phenylglyoxalate, $(C_6H_5{-}CO{-}CO_2)_2Hg$, yields metallic mercury at 180°; carbon dioxide and benzoic acid are reported products as well.

When mercuric fulminate, $Hg(ONC)_2$, is maintained [95] for 90-100 hours at 90-100°, or for 160 hours at 80°, it is converted into "pyrofulmin", which is inert and non-combustible.

Silver Salts.

Reference has already been made (p. 484) to the pyrolysis of silver acetate and its homologs. It is important to emphasize the fact that in these salts, hydrogen replaces the silver, so that

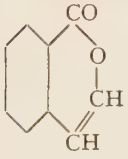
$$R{-}CO_2Ag \longrightarrow R{-}CO_2H.$$

Silver, carbon and carbon dioxide are also formed. It must be remembered that the simple aliphatic acids are unusually resistant to heat. It would be anticipated, therefore, that most silver salts would fail to give the free acid on pyrolysis, except as a transient product. In fact, it is quite generally true [96] that $R{-}CO_2Ag$ changes into $R{-}H$. Regarding the mechanism of this change, however, it is frequently difficult to see how the acid, $R{-}CO_2H$, could be even an intermediate product. For example, the silver salt [97] of *iso*carbostyril-3-carboxylic acid,  , yields a sublimate of pure *iso*carbostyril, $C_6H_4{<}\begin{matrix}CO{-}NH\\ |\\ CH{=}CH\end{matrix}$, when it is heated in an air bath at 150-160°. Since

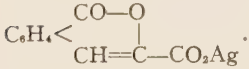
[95] Langhans, *Z. ges. Schiess-Sprengstoffw.* **17**, 9-11, 18-21, 26-28 (1922); *Chem. Abstracts* **16**, 2603 (1922).
[96] Koenigs, *Ber.* **24**, 3589 (1891); Lieben, *Ber.* **25**, 1188 (1892).
[97] Bamberger and Kitschelt, *Ber.* **25**, 1143 (1892).

*iso*carbostyril carboxylic acid does not decompose until 300-320°, it is awkward to assume that this acid is even a transient product.

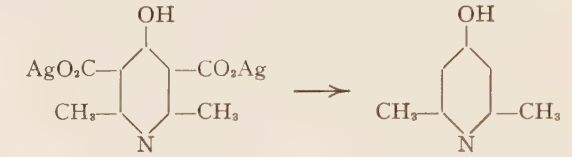
Good yields (45 percent, based on the original acid) of *iso*cumarin,[98]



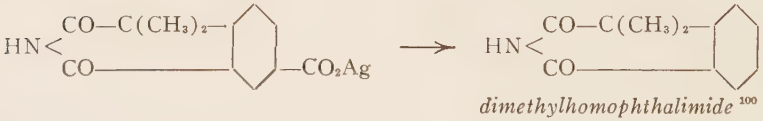
, are produced by dry-distilling silver *iso*cumarin-carboxylate,



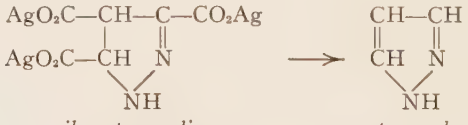
. The following cases are similar. All are effected in good yields by dry distillation.



silver orsellinate [99] *orcinol*



dimethylhomophthalimide [100]

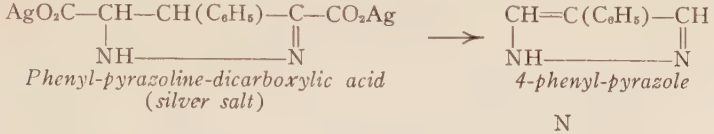


silver pyrazoline-3,4,5-tricarboxylate [101] *pyrazole*

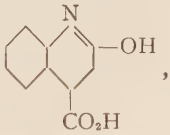
In the last case, carbon dioxide is vigorously evolved and silver remains as a residue. Traces of hydrogen cyanide are also formed. From 10 grams of the trimethyl ester, converted into the silver salt, Buchner obtained a 2 gram yield of pyrazole (theoretical yield, 3 grams). In a similar conversion [102] of the vacuum-dried silver salt of pyrazoline-3,5-dicarboxylic acid to pyrazole, the salt was mixed with a ten-fold amount of powdered clay tile before heating.

[98] Bamberger and Frew, *Ber.* **27**, 207 (1894).
[99] Cornelius and von Pechmann, *Ber.* **19**, 1451 (1886).
[100] Tiemann and Krüger, *Ber.* **26**, 2687 (1893).
[101] Buchner, *Ann.* **273**, 227 (1893).
[102] Buchner and Papendieck, *Ann.* **273**, 237 (1893).

Phenyl pyrazole may be prepared in good yields by heating the pure, neutral silver salt of phenyl-pyrazoline-dicarboxylic acid:[103]



Phenyl-pyrazoline-dicarboxylic acid (silver salt) → *4-phenyl-pyrazole*

If 5 grams of α-hydroxycinchoninic acid,  , is transformed[104] into its silver salt, and the latter dried and heated, 2 grams of carbostyril distils. The acid silver salt of α-ethoxycinchoninic acid also decomposes smoothly in a combustion tube into ethyl-carbostyril, if the decomposition is performed in a carbon dioxide atmosphere; and in like fashion, α-hydroxypyridine (α-pyridone) may be formed[105] from the acid silver salt of α-hydroxyquinolinic acid, $C_6H_2(OH)N\begin{cases}CO_2H\\CO_2Ag\end{cases}$.

The silver salt of acetylene dicarboxylic acid[106] is incapable of existence, as shown by the following equation which occurs quantitatively in water solution:

$$NaO_2C{-}C{\equiv}C{-}CO_2Na + 2AgNO_3 \longrightarrow Ag{-}C{\equiv}C{-}Ag + 2NaNO_3 + 2CO_2.$$

Another non-existent silver salt, $[N{\equiv}C{-}CO_2Ag]$, shares a common grouping, $({\equiv}C{-}CO_2Ag)$.

That copper salts may also be instrumental in the decarboxylation by thermal means is evident from the work of Dougherty, who showed that if *o*-benzoyl-benzoic acid is mixed with one-fifteenth of its weight of the copper salt of this acid[107] and maintained at 260° for four hours a yield of 82-84 percent of benzophenone may be realized.

Salts of Dibasic Acids.

Calcium malonate possesses interesting undeveloped possibilities for study. From the anhydrous salt, one would expect ketene to be formed by pyrolysis, according to the equation:

$$CH_2\begin{cases}CO_2\\CO_2\end{cases}Ca \longrightarrow CH_2{=}C{=}O + CaCO_3.$$

[103] Buchner and Papendieck, *Ber.* **28**, 223 (1895).
[104] Koenigs and Koerner, *Ber.* **16**, 2153 (1883).
[105] *Ibid.* p. 2158; *also*, Koenigs and Geigy, *Ber.* **17**, 590 (1884).
[106] Lossen, *Ann.* **272**, 140 (1893).
[107] Dougherty, *J. Am. Chem. Soc.* **50**, 571 (1928).

Dry distillation of calcium succinate [108] produces very small quantities (0.4 gram from 1 kilogram) of cyclohexanedione,

$$OC<\begin{matrix}CH_2—CH_2\\ \\ CH_2—CH_2\end{matrix}>CO$$

This must have been formed through the residue, $[—CH_2—CH_2—CO—]$, from $\begin{matrix}CH_2—CH_2—CO\\ |\quad\quad\quad\quad|\\ CO—O—Ca—O\end{matrix}$, which has been postulated in another connection (p. 404) to explain the pyrolytic products from succinic anhydride.

Small yields of anthraquinone,[109] presumably formed in a manner identical to cyclohexanedione, result from the pyrolysis of calcium phthalate:

$$2C_6H_4<\begin{matrix}CO_2\\ \\ CO_2\end{matrix}>Ca \longrightarrow C_6H_4<\begin{matrix}CO\\ \\ CO\end{matrix}>C_6H_4 + 2CaCO_3$$

Similarly,[110] calcium tetrachlorophthalate, $C_6Cl_4<\begin{matrix}CO_2\\ \\ CO_2\end{matrix}>Ca$, changes on distillation into octachloro-anthraquinone.

Calcium succinate does not yield cyclopropanone on distillation; neither does calcium glutarate furnish cyclobutanone. This property of changing into a simple cyclic ketone begins in the adipic series, and continues in the higher homologs.

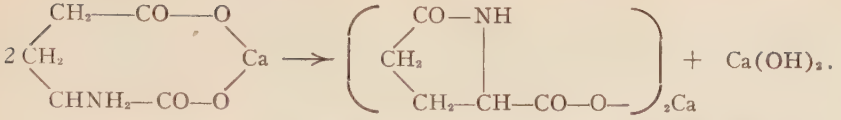
In the glutaric series, barium β,β-dimethylglutarate,

$$(CH_3)_2C<\begin{matrix}CH_2CO_2\\ \\ CH_2CO_2\end{matrix}>Ba$$

yields [111] especially acetone, mesityl oxide and *iso*phorone, as it is heated in the dry state. Mesityl oxide is isomeric with dimethyl*cyclo*butanone, which may be considered as primarily formed. The formation of acetone is explained experimentally by the reaction at high temperatures between mesityl oxide and barium carbonate, in the presence of traces of water. *Iso*phorone then comes by the reaction of acetone with mesityl oxide.

Calcium glutamate,[71] an amino derivative, changes into calcium pyrrolidone carboxylate at 180-185°. This indicates the following equation:

[108] Feist, *Ber.* **28**, 739 (1895).
[109] Panaotovits, *Ber.* **17**, 312 (1884).
[110] Kircher, *Ber.* **17**, 1170 (1884).
[111] Windaus and Ehrenstein, *Nach. kgl. Ges. Wiss. Göttingen, Math-physik. Klasse* **1922**, 1; *Chem. Abstracts* **17**, 1431 (1923).



While not strictly a thermal degradation, the following method of passing from a glutarate to a γ-lactone is of sufficient interest and importance to be mentioned here. It has already been shown that compounds in the glutaric series decompose smoothly by heat into anhydrides, but little is known concerning the pyrolysis of the latter. Little also is known concerning the pyrolysis of the salts. The following method of degradation [112] starts with a silver salt, $CH_2(CH_2{-}CO_2Ag)_2$, in the glutaric series. It is finely ground with an equivalent amount of iodine, mixed with sand, and then heated. Either the anhydride, $\begin{matrix} CH_2{-}CH_2{-}CO \\ | \quad\quad | \\ CH_2{-}CO{-}O \end{matrix}$ or the lactone, $\begin{matrix} CH_2{-}CH_2{-}CO \\ | \quad\quad | \\ CH_2{-}\quad{-}O \end{matrix}$, is formed (together with carbon dioxide) in this reaction. The yield of lactone depends on the constitution of the glutaric acid used and on the temperature, and ranges up to 40 percent. In this way, glutaric acid gives 30 percent of γ-butyrolactone; β,β-dimethylglutaric acid gives 40 percent of β,β-dimethyl-γ-butyrolactone; α-ethylglutaric acid gives γ-caprolactone, and no α-ethyl-γ-butyrolactone, which indicates that the carbon dioxide is split off much more easily from the tertiary than from the secondary carbon.

Since this reaction does not occur with succinates, it becomes a valuable reaction in qualitative organic analysis. To determine the position of carboxyl groups in an aliphatic dicarboxylic acid, the acid is evaporated with acetic anhydride and heated at 260-280°. A smooth transformation into a ketone will indicate a pimelic or adipic acid, whereas a smooth change into an anhydride, stable at this temperature, will indicate a glutaric or succinic acid. In the latter case, the silver salt is heated with iodine, the formation of a lactone indicating the presence of the glutaric functional group.

The following two reactions [113] are added for reference:

$$2R{-}CHOH{-}CO_2Ag + I_2 \longrightarrow 2AgI + R{-}CHOH{-}CO_2H + CO_2 + RCHO.$$

$$2R_2COH{-}CO_2Ag + I_2 \longrightarrow 2AgI + R_2C(OH){-}CO_2H + CO_2 + R_2CO.$$

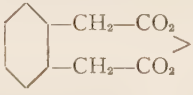
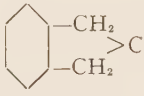
Both reactions take place with ease, and the aldehyde or ketone is readily isolable.

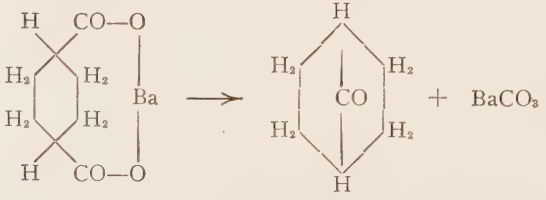
[112] Windaus and Klanhardt, *Ber.* **54**, 581 (1921).
[113] Herzog and Leiser, *Monatsh.* **22**, 357 (1901).

Calcium adipate, like adipic acid, gives cyclopentanone [114] when heated. Ruzicka reported a 43 percent yield. Cyclopentanone is best prepared from barium adipate at 290°; the yield [115] is 75-80 percent of the theoretical:

$$(CH_2)_4\begin{matrix}CO{-}O\\ \\ CO{-}O\end{matrix}\!>Ba \longrightarrow \begin{matrix}CH_2{-}CH_2\\ |\quad\quad >CO\\ CH_2{-}CH_2\end{matrix} + BaCO_3.$$

The lead salt of adipic acid [114] gives a 35 percent yield, and the thorium salt a 15 percent yield. No ketone (cyclobutanone) whatsoever results from heating thorium glutarate.

This reaction is general. An aromatic nucleus may share the carbons in the adipic chain providing that only *ortho* carbon atoms participate. In accordance with Bredt's rule (p. 12), *meta* or *para* carbons in the chain may not participate since they would demand a *meta* or *para* ring closure. Thus, whereas 100 grams of the calcium salt of *o*-phenylenediacetic acid,[116]  , produces about 15 grams of *β*-hydrindone,  , on heating, this behavior is not shown in the *m*- and *p*- isomers. By supplying a cyclohexane nucleus instead of a benzene nucleus, the objection of Bredt's rule for the *m*- and *p*- compounds is no longer valid since no double bonds would appear at the cyclic junctions. Actually, the barium salt of hexahydroterephthalic acid yields a compound on distillation which is probably bicyclo-1,2,2-heptanone.[117] Considerable quantities of hydrogen and benzene are also formed.

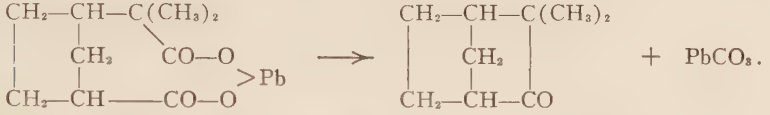


It should be pointed out that hexahydroterephthalic acid and adipic acid possess the same functional group.

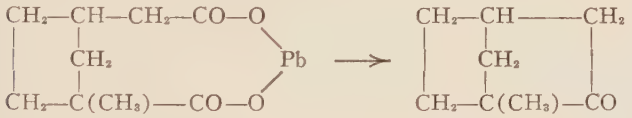
Other salts of fully reduced cyclic dibasic acids which are similarly related to adipic acid, and which should give a ketonic ring-closure on

[114] Ruzicka and others, *Helv. Chim. Acta* **9**, 514 (1926).
[115] Thorpe and Kon, "Organic Syntheses," Vol. V, New York, John Wiley and Sons, **1925**, p. 37.
[116] Schad, *Ber.* **26**, 222 (1893); Wislicenus and Benedikt, *Ann.* **275**, 352 (1893).
[117] Zelinsky, *Ber.* **34**, 3798 (1901).

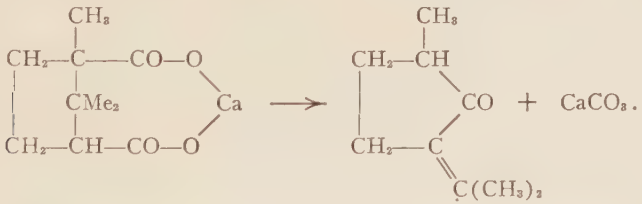
heating, occur in the terpenes. Distillation of lead camphene-camphorate [118] in a current of carbon dioxide yields camphenilone. The reaction is accompanied by much swelling. The calcium salt fails to give the reaction.



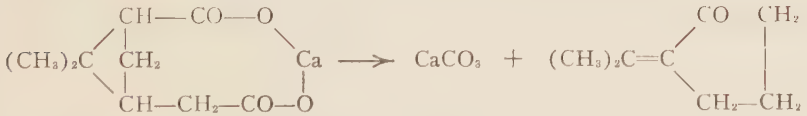
The following reaction, employed by Ruzicka [119] in the synthesis of fenchone, is practically identical. Distillation of the lead salt of methyl-*nor*-homocamphoric acid (in a current of carbon dioxide) in 5 gram portions yields 1.5 grams of a crude oil which consists chiefly of methyl-*nor*-camphor.



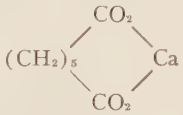
Pyrolysis of calcium camphorate [120] leads to camphorphorone, an isomer of the bicyclic ketone which might be anticipated:



Analogous to this is the pyrolytic conversion of calcium pinate [121] into *iso*propylidene-2-cyclopentanone:



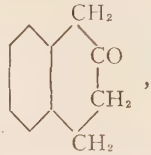
Cyclohexanone may be made [122] from calcium pimelate,



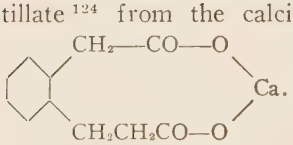
[118] Komppa and Hintikka, *Ber.* **47**, 1550 (1914).
[119] Ruzicka, *Ber.* **50**, 1372 (1917).
[120] Gerhardt and Liès-Bodart, *Ann.* **72**, 293 (1849); Fittig, *Ann.* **112**, 311 (1859); Semmler, *Ber.* **25** 3520 (1892).
[121] Bonsdorff, *Ber.* **44**, 3208 (1911).
[122] Wislicenus and Mager, *Ann.* **275**, 361 (1893).

by dry distillation. The thorium salt [114] gives 70-80 percent of cyclohexanone, a result which is in marked contrast to the 15 percent yield of cyclopentanone from thorium adipate. Of course, cyclohexanone is much more readily made from cyclohexanol, so that this reaction is of scientific interest only. The racemic form of methyl-1-cyclohexanone-3 is similarly synthesized [123] from the calcium salt of β-methylpimelic acid:

The salt of γ-methylpimelic acid pyrolyzes in analogous fashion. Likewise, β-ketotetrahydronaphthaline,

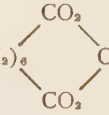


, is in the distillate [124] from the calcium salt of *o*-phenyleneacetic-propionic acid,



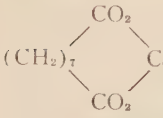
Cyclic ketones with seven to eighteen carbons in the ring may also be prepared by the pyrolysis of salts of the suitable dibasic acid, but the yields diminish appreciably. The best yields are realized in the preparation of 5- or 6-membered rings. Ruzicka concludes [125] that on the basis of their relative ease of formation, the carbon rings, exclusive of double bonds, may be arranged in three classes: 5- and 6- rings; 3-, 4- and 7-rings; 8- and higher rings. The carbon-to-carbon double bond (2-ring) possesses a greater ease of formation than any ring compound. The "ease of formation" is, therefore, not proportional to the "stability" of the ring system (compare 3-, 4- and 7-), as has so often been assumed as a result of the Baeyer strain theory.

When calcium suberate,

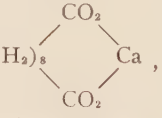


, is heated [126] at a temperature of 375-400° and 10 mm. pressure in a horizontal tube, cycloheptanone distils in a 30-34 percent yield. The thorium or the cerium salt of suberic acid [114] gives a 45 percent yield.

[123] Einhorn and Ehret, *Ann.* **295**, 181 and 186 (1897).
[124] Einhorn and Lumsden, *Ann.* **286**, 275 (1895).
[125] Ruzicka and others, *Helv. Chim. Acta* **5**, 499 (1926).
[126] Godchot, *Compt. rend.* **171**, 1387 (1920); Wislicenus and Mager, *Ann.* **275**, 357 (1893).

Just as calcium suberate yields cycloheptanone, calcium azelate,  , gives rise to cyclooctanone.[127] However, Harries and Fork demonstrated that the reaction product contained not only cyclooctanone but also methylated cyclo-pentanones, -hexanones, and -heptanones. Further work by Ruzicka and Brugger [128] demonstrated the formation of about 10 percent of the theoretical yield of cyclooctanone from the *calcium* or the *cerium* salt, and about 2 percent from the *lead* or the *zirconium* salt. The *thorium* salt gives rise to a 20 percent yield, the details of which follow.

Azelaic acid (325 grams) is neutralized with 20 percent sodium hydroxide solution, and is then precipitated as the thorium salt with 500 grams of thorium chloride ($ThCl_4$) (in water). The salt is collected on a filter, washed, dried at 150°, and then distilled in three portions from a copper retort. The distillate, after being freed from acidic components by an alkaline wash, weighs 144 grams. Fifteen grams of this boils between 100-175° at 730 mm., and the remainder is distilled at 12 mm. Ten grams is collected between 65-75°; 44 grams, chiefly cyclooctanone, between 75-90°; and 5.5 grams between 90-120°. At 12 mm. pure cyclooctanone boils at 74°. A small quantity of cyclooctanone may be isolated from the first fractions of this distillate.

Many years ago, Calvi [129] heated calcium sebacate,  , but from the distillate he could isolate no known products. Later, Petersen [130] identified propionaldehyde, heptaldehyde, small amounts of benzene, and a solid hydrocarbon, sebacin, probably $C_{20}H_{18}$. Zelinsky [131] was the first to identify cyclononanone from calcium sebacate, and his yield was about 0.9 percent. Twenty grams of crude cyclononanone, or 9 grams of the purified product, came from 1 kg. of sebacic acid. The thorium salt gives 1.5 percent of cyclononanone, which is slightly better. One kilogram of thorium sebacate,[132] distilled in portions from a copper retort at temperatures up to 500° and under diminished pressure, gives 160 grams of a neutral distillate which can be fractionated into a 34 gram portion, boiling point (12 mm.) 40-75°, and a 50 gram por-

[127] Wislicenus and Mager, *Ann.* **275**, 363 (1893); Harries and Fork. *Ber.* **40**, 4555 (1907).
[128] Ruzicka and Brugger, *Helv. Chim. Acta* **9**, 339 (1926).
[129] Calvi, *Ann.* **91**, 110 (1854).
[130] Petersen, *Ann.* **103**, 184 (1857).
[131] Zelinsky, *Ber.* **40**, 3277 (1907).
[132] Ruzicka, Stoll and Schinz, *Helv. Chim. Acta* **9**, 249 (1926); Ruzicka and Brugger, *ibid.* p. 389; Ruzicka and others, *ibid.*, **11**, 496, 670, 686 (1928).

tion, boiling point (12 mm.) 75-115°. These fractions give 20 grams of a semicarbazone mixture that includes suberone, methyl octyl ketone and cyclononanone. This is a 3 percent yield of total ketones.

Cyclodecanone [132] is similarly prepared, but in still smaller yields, namely, 0.1-0.2 percent, from the thorium salt of nonane-1,9-dicarboxylic acid. All the intermediate carbocyclic ketones to cyclooctadecanone inclusive, $(CH_2)_{17}CO$, have been synthesized by similar pyrogenic methods. As will be seen from the table below, the yields of $(CH_2)_{14}CO$, $(CH_2)_{16}CO$ and $(CH_2)_{17}CO$ constantly increase, but in all cases are decidedly better than with $(CH_2)_9CO$.

TABLE XLVI. *Pyrogenic Synthesis of Carbocyclic Ketones from Thorium Salts of Dicarboxylic Acids.*

Dicarboxylic Acid	Weight Grams	End Product	Weight Grams
Nonane-dicarboxylic acid ...	196	Cyclodecanone fraction	2.2
Tetradecane-dicarboxylic acid	100	Cyclopentadecanone (exaltone) fraction	7.1
Hexadecane-dicarboxylic acid	48	Cycloheptadecanone (dihydrocivetone) fraction	5.9
Heptadecane-dicarboxylic acid	95	Cyclooctadecane fraction	22

On the basis of 100 grams of original dibasic acid in each case, the yields of cyclic ketones, respectively, would be 1.1, 7.1, 12.3 and 23 grams. In percentage yields, these values would become 1.5, 9.1, 15.3 and 28.4 percent respectively. It must be realized that the yield of purified ketone is considerably less in each case.

The synthesis of this type of compound opens the field for the technical preparation of natural musk and civet odorous principles. Cyclodecanone and cyclododecanone distinctly possess the odor of camphor; the ketone with 13 carbon atoms has a slight cedar-wood odor, as have the concentrated forms of the higher ketones. When diluted, the ketones with 14-18 carbon atoms have a characteristic musk odor,[133] which is most noticeable with the 15-carbon atom ketone, "exaltone". Civetone, $\begin{matrix} CH—(CH_2)_7—CO \\ \| \qquad\qquad\quad | \\ CH—(CH_2)_6—CH_2 \end{matrix}$, is an odorous component of civet,[134] which is present to the extent of about 3 percent. This is of interest because it is a seventeen membered ring and perhaps shows the biological origin of the material from oleic acid. Dihydrocivetone, therefore, is cycloheptadecanone. Civetone may be prepared by the vacuum distillation (0.3 mm.) of commercial civet. If 100 gram samples are taken, about 8 gram yields are realized.

[133] M. Naef et Cie, Brit. Pat. 235,540, June 16, 1924; Brit. Pat. 251,188, May 18, 1925; *Chem. Abstracts* **20**, 917 (1926); **21**, 1272 (1927).
[134] Ruzicka, *Helv. Chim. Acta* **9**, 230 (1926).

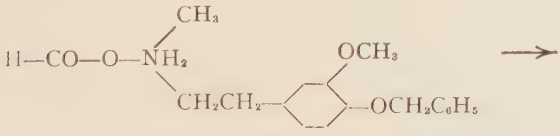
Ammonium Salts.

Because of the relationship of nitrile, amide, and ammonium salt, the ammonium salts differ quite materially from the metallic salts in their thermal decompositions. Quite customarily they are dehydrated by heat into amides, but only rarely does the reaction proceed to the nitrile. Furthermore, there is usually more or less of a tendency for the salt to dissociate into ammonia and the acid. If troublesome, this dissociation may frequently be minimized by the presence of excess acid, or by the use of a sealed tube.

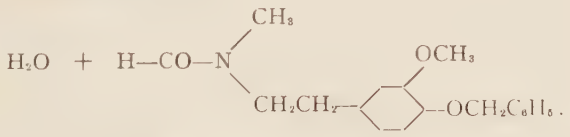
Ammonium Salts of Monobasic Acids.

Ammonium formate [135] melts with decomposition at 114°, yielding not only formamide and water, but also small amounts of hydrocyanic acid. This is one of the few cases wherein a nitrile has been observed as a decomposition product of an ammonium salt. In the distillation of ammonium formate at atmospheric pressure,[136] ammonia and water are liberated at about 100°, formic acid at 150°, and at 185-190° formamide becomes the leading product of the distillation. In turn, formamide starts to pyrolyze into carbon monoxide and ammonia, and into water and hydrogen cyanide or ammonium cyanide. This is especially noticeable after the temperature of the vapors exceeds 195°.

The dehydration [137] of the following disubstituted derivative of ammonium formate, $HCO_2NH_2R_2$, into a disubstituted formamide, $HCONR_2$, occurs at 170-175°:



methyl-β-(3-methoxy-4-benzyloxy-phenyl)-ethylammonium formate



formylmethyl-β-(3-methoxy-4-benzyloxy-phenyl)-ethylamine

One of the best known preparative methods for *acetamide* is the pyrolysis of *ammonium acetate*. Acetonitrile does not appear as a by-

[135] Andreasch, *Ber.* **12**, 973 (1879); Curtius and Jay, *J. prakt. Chem.* [2] **39**, 34 (1889).
[136] Freer and Sherman, *Am. Chem. J.* **20**, 224 (1898).
[137] Akabori, *Bull. chem. soc. (Japan)* **1**, 96 (1926); *Chem. Abstracts* **21**, 96 (1927).

product, but dissociation into ammonia and acetic acid is encountered, which is best avoided either by a sealed tube reaction, or, preferably, by a slow distillation [138] of a mixture of equivalent amounts of ammonium acetate and glacial acetic acid. In the latter case, the excess of acid undoubtedly serves to retain the ammonia which otherwise might escape, but this is not its only function. It is also definitely catalytic.

The percentage of acetamide [139] formed when ammonium acetate is heated alone in a sealed tube is given in Table XLVII.

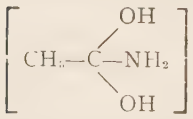
TABLE XLVII. *Speed of Formation of Acetamide from Ammonium Acetate.*

Temperature °C.	Acetamide in 1 Hour Percent	Acetamide at Equilibrium Percent
125	6.33	75.10
137	17.14	77.05
140	21.36	78.18
152.5	44.07	79.00
155	50.90	81.46
182.5	78.31	82.82
212.5	82.83	84.04

In Table XLVIII [140] is shown the effect of a constant temperature, with time as the variable.

TABLE XLVIII. *Speed of Formation of Acetamide from Ammonium Acetate.*

Time in Hours	Acetamide Percent at 137°	at 155°	at 182.5°	at 212.5°
0.5	9.11	....	....	....
1.0	17.14	50.9	78.31	82.83
2.0	28.83	....	....	....
4.0	....	78.1	....	....
4.33	45.66	....	....	....
12.0	....	....	....	83.96
24.0	65.40	80.6	82.60	....
50.0	76.93	....	....	....
Equilibrium	77.05	81.6	82.82	84.04

The formation of acetamide from ammonium acetate is essentially a dimolecular reaction between ammonia and acetic acid, and Noyes and Goebel postulate the formation of an intermediate compound,  , as an ephemeral step in the process. This is preceded either by dissociation into "ammonia + acetic acid", or into "ammonia + $CH_2{=}C(OH)_2$". Some evidence for the latter is the fact [141] that

[138] Noyes and Goebel, *J. Am. Chem. Soc.* **44**, 2295 (1922).
[139] Noyes and Goebel, *J. Am. Chem. Soc.* **44**, 2290 (1922); Menschutkin, *J. prakt. Chem.* **29**, 445 (1884).
[140] Noyes and Goebel, *J. Am. Chem. Soc.* **44**, 2288 (1922).
[141] Menschutkin, *J. prakt. Chem.* **29**, 432, 435 (1884).

ammonium benzoate and ammonium anisate, which cannot pass into the enol form, are converted into the amides very slowly indeed.

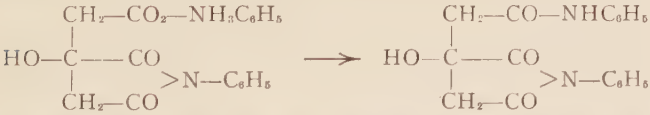
It may not be amiss to mention Reik's work [142] on the behavior of ammonium salts when heated under diminished pressure. Ammonium acetate undergoes a partial decomposition into an acid salt, $(CH_3CO_2)_2H.NH_4$. If pure, this acid-salt may be sublimed or distilled in a vacuum. Similarly, ammonium propionate yields $(C_2H_5CO_2)_2H.NH_4$, whereas ammonium *iso*valerate was reported to yield principally the diacid salt, $NH_4C_5H_9O_2.2C_5H_{10}O_2$.

The results of an investigation [143] on speeds of reaction of several ammonium salts, when heated in a sealed tube, are presented in Table XLIX.

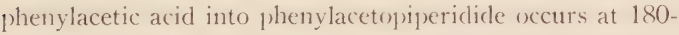
Reference has already been made (p. 490) to the behavior of the ammonium, and of the diethylammonium, salts of β-phenyl-β-bromopropionic acid, thus demonstrating the effect of a β-halogen atom.

The familiar conversion of a mixture of aniline and glacial acetic acid into acetanilide by a few hours' refluxing [144] indicates the similarity of phenylammonium acetate to ammonium acetate in this type of reaction. In practice, it is recommended [145] to employ an upright air condenser, fitted at the top with a thermometer and an exit tube. The mixture in the flask is boiled at such a rate that the thermometer registers 105°. Water and some acetic acid are driven off; in about 2 hours, the process is complete.

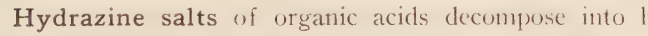
The aniline salt of citranilic acid [146] melts at 139°; at 150° it decomposes into the anil-anilide of citric acid in 30 minutes:



This compound may also be prepared [147] by heating the dianiline salt of citric acid. The transformation [148] of the piperidinium salt of phenylacetic acid into phenylacetopiperidide occurs at 180-200°:



Hydrazine salts of organic acids decompose into hydrazides by heat:



[142] Reik, *Monatsh.* **23**, 1033 (1902).
[143] Menschutkin, *loc. cit.; also Compt. rend.* **98**, 1049 (1884).
[144] Williams, *J. Chem. Soc.* **2**, 106 (1864).
[145] For example, *see* Cohen, "Practical Organic Chemistry," New York, Macmillan Co. 1924, p. 169.
[146] Nau, Brown and Bailey, *J. Am. Chem. Soc.* **47**, 2601 (1925).
[147] Pebal, *Ann.* **82**, 92 (1852); **98**, 83 (1856).
[148] Wislicenus and Erbe, *Ann.* **421**, 119 (1920).

TABLE XLIX. *Speed of Formation of Amides from Ammonium Salts.*
(A = percent amide in 1 hour; B = percent amide at equilibrium)

Amide from	125° A	125° B	140° A	155° A	155° B	182.5° A	182.5° B	212.5° A	212.5° B
Ammonium formate	23.41	52.25	....	57.46	....	....	....	....	....
" acetate	6.33	75.10	21.36	50.90	81.46	78.31	82.82	82.83	84.04
" propionate	....	....	....	50.93	84.71	....	84.26	....	85.43
" butyrate	....	....	....	42.46	84.13	....	....	82.24	82.58
" *iso*butyrate	0.0	77.87	17.20	37.09	84.67	74.32	83.79	81.51	83.66
" capronate	4.74	78.08	....	48.17	84.33	76.07	82.71	80.78	82.41
" phenylacetate	....	....	....	36.4	81.5	....	....	....	....
" benzoate	....	....	....	0.75	8.82	....	....	....	....
" anisate	....	....	....	3.8	....	....	....	....	....

Thus, acetohydrazide, in 95 percent yields, is produced after 2 days' heating of hydrazonium acetate [149] on the steam bath. Propionhydrazide is prepared in 92 percent yield, and similarly the lactate may be changed into lactic hydrazide. There is a tendency for the hydrazides of the aromatic acids to pyrolyze further, giving the symmetrical diarylhydrazides, Ar—CO—NH—NH—CO—Ar. This is a rather inappreciable effect in the case of hydrazonium benzoate (which gives benzohydrazide after 8 hours' heating at 100°), but is the sole reaction with the salt of *p*-bromobenzoic acid. The *p*-toluate gives a mixture of the mono- and di-*p*-toluyl hydrazides.

The **hydroxylamine salts** of aliphatic acids also lose a molecule of water by heating, thereby producing hydroxamic acids.[150] The general equation is:

$$R—CO—O—NH_3OH \longrightarrow R—CO—NHOH + H_2O.$$

Thus, the formate gives formohydroxamic acid; the acetate, acetohydroxamic acid, etc. An equilibrium value, comparable to that which was noticed in the conversion of ammonium acetate to acetamide, cannot be realized because of the fact that the hydroxamic acids decompose further at the temperature of the reaction.

Hydroxylamine formate melts at 76°. A test with ferric chloride solution reveals the fact that dehydration to formohydroxamic acid definitely occurs at 78-80°, but at 80° a violent decomposition sets in, giving gaseous products. With hydroxylamine acetate at 90°, a fairly successful synthesis of acetohydroxamic acid may be effected. In one hour, a 2 gram sample gives a 28 percent yield; in 3.5 hours, a 30.6 percent yield. Longer heating diminishes the yield (thus, 24.9 percent in 4.5 hours), because of contending pyrolytic reactions.

Whether or not the same mechanism applies for hydroxylammonium acetate that was proposed (p. 508) for ammonium acetate cannot be stated. Such a mechanism would involve the following steps:

$$CH_3—CO_2—NH_3OH \longrightarrow \left[CH_3—C(OH)(NHOH)—OH \right] \longrightarrow CH_3—CO—NHOH + H_2O.$$

Ammonium and hydroxylammonium salts have a point in common; namely, the salts of either type in the aromatic series show very little disposition to undergo this general reaction. The hydroxylamine salts

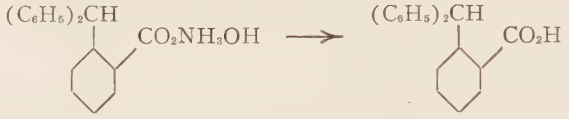
[149] Curtius and Franzen, *Ber.* 35, 3241 (1902).
[150] Jones and Oesper, *Am. Chem. J.* 42, 517 (1909).

of the aromatic acids [151] do not give hydroxamic acids on heating. Instead, they appear to dissociate into the free acid and hydroxylamine or its decomposition products. Since ammonia is one of the decomposition products of hydroxylamine, part of it will be retained as the ammonium salt of the acid.

$$Ar{-}CO{-}O{-}NH_3OH \longrightarrow Ar{-}CO_2H + [NH_2OH] \xrightarrow{NH_3,\ \text{etc.}} \text{(see p. 658)}$$

$$Ar{-}CO_2H + NH_3 \longrightarrow Ar{-}CO_2NH_4$$

Only the free acid is isolable [152] in the case of hydroxylammonium *o*-benzohydrylbenzoate at 150°. The gases which escape contain ammonia.



The hydroxylamine salts of succinic, fumaric and succinamic acids have been prepared and subjected to pyrolysis. Only the latter appears to behave normally and give the hydroxamic acid,[153] and it may be pointed out that only the latter is derived from a monobasic acid:

$$H_2N{-}CO{-}C_2H_4{-}CO_2NH_3OH \longrightarrow H_2N{-}CO{-}C_2H_4{-}CONHOH + H_2O.$$

Hydroxylamine succinate [154] undergoes a curious decomposition into $HO_2C{-}CH_2{-}CH_2{-}CO{-}N{=}N{-}CO{-}CH_2{-}CH_2{-}CO_2NH_4$ (?), and nitrogen (see p. 678). Hydroxylamine fumarate decomposes in warm aqueous solutions [155] into the ammonium salt of aspartic acid, and in fairly good yields. Tanatar gives the following equation:

$$3HONH_3{-}O{-}CO{-}CH{=}CH{-}CO{-}O{-}NH_3OH \longrightarrow H_2N{-}O{-}CO{-}CH(NH_2){-}CH_2{-}CO_2NH_4 + 4CO_2 + 2H_2O.$$

Water is eliminated at 100-110° from the hydroxylammonium salt of benzene sulfinic acid, not with the formation of benzenesulfinhydroxamic acid, however. Benzenesulfonamide [156] is the product of the reaction:

$$C_6H_5{-}SO{-}O{-}NH_3OH \longrightarrow H_2O + C_6H_5{-}SO_2{-}NH_2.$$

Ammonium carbamate, $H_2N{-}CO{-}O{-}NH_4$, changes into urea by heating. Basarov [157] originally induced this change by heating at 130-

[151] Oesper and Ballard, *J. Am. Chem. Soc.* **47**, 2425 (1925).
[152] Jones and Root, *J. Am. Chem. Soc.* **48**, 190 (1926).
[153] Ssabanejeff, *Chem. Zentr.* **1899**, II, 33.
[154] Tanatar, *Chem. Zentr.* **1897**, II, 68, 339 and 659.
[155] Tanatar, *Ber.* **29**, 1478 (1896).
[156] Whalen with Jones, *J. Am. Chem. Soc.* **47**, 1356 (1925).
[157] Basarov, *J. prakt. Chem.* [2] **1**, 283 (1870).

140° in a sealed tube. Although outwardly this resembles a simple dehydration, and for many years it was so regarded, Werner has submitted evidence [158] to show that this simple mechanism is far from the truth. He has demonstrated that urea is not "carbamide", and that urea formation must invariably be preceded by the formation of *iso*cyanic acid. Part of the evidence on which this is based is the fact that substituted ureas are formed from substituted ammonium carbamates only when there is a possibility of intermediate *iso*cyanate formation. The following equations make this clear.

$$RNH{-}CO{-}O{-}NH_3R \longrightarrow [RNH{-}CO_2H] + RNH_2$$

The substituted carbamic acid may then decompose in one of two ways:

$$[RNH{-}CO_2H] \begin{cases} \nearrow RNH_2 + CO_2 \\ \searrow R{-}N{=}C{=}O + H_2O \end{cases}$$

The *iso*cyanate may then accept an amine molecule, yielding the urea:

$$R{-}N{=}C{=}O + RNH_2 \longrightarrow RNH{-}CO{-}NHR.$$

These equations agree well with the facts, since carbon dioxide, water and amine are all produced as well as the urea. In fact, if ammonium carbamate is heated only to 60° in an open vessel, ammonia and carbon dioxide are evolved. A clinching argument, however, against simple dehydration of the carbamate is furnished with ammonium salts of disubstituted carbamic acid. Were it only necessary to expel a molecule of water by thermal means, these salts should also be precursors of ureas. Actually, ureas are never observed, nor should they be since an examination of the formula shows that there is no possibility of decomposition into an intermediate molecule of isocyanate:

$$R_2N{-}CO{-}O{-}NH_3R \longrightarrow [R_2N{-}CO{-}OH] + RNH_2.$$
$$\downarrow$$
$$R_2NH + CO_2$$

The only products of the reaction are amines and carbon dioxide.

In the commercial transformation [159] of ammonium carbamate into urea, 200 kilograms of the salt is heated 2 to 4 hours in an autoclave at 150°. Seventy kilograms of urea (about 48 percent of the theory) is reported, as well as carbon dioxide, ammonia and water. In a study of the optimum conditions for the preparation of urea from ammonium carbamate, Fichter and Becker [160] heated 4 gram samples of ammonium

[158] Werner, *J. Chem. Soc.* **117**, 1046 (1920).
[159] Matignon and Fréjacques, *Chimie et industrie* **7**, 1057 (1922).
[160] Fichter and Becker, *Ber.* **44**, 3475 (1911).

carbamate in a tin-lined steel bomb of 37 cc. capacity. Apparently, 135° is the optimum temperature regardless of the duration of heating.

TABLE L. *Effect of Temperature on Yield of Urea from Ammonium Carbamate.*

Temperature of Bomb °C.	Yield of Urea Percent in 24 Hours	in 48 Hours
115	0.65	....
120	5.20	8.75
130	28.18	30.06
135	30.07	31.20
140	28.06	27.96
150	24.28	....

Other factors influence the yield as well, one of which is the quantity of material taken, as the following table reveals. The 37 cc. reaction tube was used throughout, and the temperature for all experiments was 135°.

TABLE LI. *Effect of Varying Quantity of Material Taken on Yield of Urea from Ammonium Carbamate.*

Weight of Ammonium Carbamate Taken Grams	Duration of Heating Hours	Yield of Urea Percent
1.2	24	traces
2.0	24	13.6
3.0	24	28.0
4.0	48	31.2
8.0	48	36.6
16.0	48	36.7
16.0	72	40.0
24.0	96	40.64

In accord with the theoretical considerations mentioned above, dimethylammonium benzylcarbamate,[161] $C_6H_5CH_2NH—CO—O—NH_2(CH_3)_2$, changes into benzyl dimethyl carbamide, $C_6H_5CH_2—NH—CO—N(CH_3)_2$, after 4 hours at 140-150°. The diethylammonium analog functions also in this manner, but methylammonium diethylcarbamate, $(C_2H_5)_2N—CO—O—NH_3CH_3$, gives no methyl diethyl carbamide. Fichter and Becker obtained similar positive results with carbamates [162] of the general formula, $RNH—CO—O—NH_3R$, wherein R represents methyl, ethyl or benzyl, but obtained negative results from diethylammonium diethylcarbamate, $(C_2H_5)_2N—CO—O—NH_2(C_2H_5)_2$.

When substituted ureas are formed in this way, the yields depend on the duration of heating and on the temperature. The yields are of a similar order of magnitude to the yields of urea from ammonium carbamate. The results are tabulated below. These data were obtained on 2 gram samples heated in a sealed tube of 6-8 cc. capacity.

[161] Werner, *J. Chem. Soc.* **117**, 1048 (1920).
[162] Fichter and Becker, *Ber.* **44**, 3481 (1911).

TABLE LII. *Effect of Temperature and Duration of Heating on the Formation of Substituted Ureas.*

Temp. °C.	Duration of Heating Hours	Symmetrical Dimethyl Urea from $CH_3NHCO_2NH_3CH_3$	Symmetrical Diethyl Urea from $C_2H_5NHCO_2NH_3C_2H_5$	Symmetrical Dibenzyl Urea from $C_7H_7NHCO_2NH_3C_7H_7$
		Percent		
120	20	none	8.09	...
130	20	10.8	16.17	...
130	40	...	24.26	...
140	20	15.6	....	...
140	40	...	48.54	...
150	20	31.2	51.98	39.8
150	40	57.6	58.91	...
160	20	54.0	45.63	47.3
160	40	65.0	46.78	...
170	20	68.4	32.35	52.7
180	20	66.0	....	55.9
180	40	...	....	58.0

Benzohydrylammonium benzohydrylcarbamate,[163] $(C_6H_5)_2CHNH—CO—O—NH_3CH(C_6H_5)_2$, behaves uniquely. If heated in a sealed tube at 180-200° it gives none of the urea, but instead ammonia is evolved and tribenzohydrylamine, $((C_6H_5)_2CH)_3N$, is formed. See p. 296.

Except for the high yield of carbohydrazide which is produced, the *hydrazine salt* of *hydrazine-monocarboxylic acid* resembles the ammonium salt of carbamic acid in its behavior towards heat. Long refluxing [164] at 140° produces nearly quantitative yields (97.7 percent):

$$NH_2—NH—CO—O—NH_3—NH_2 \longrightarrow CO(NH—NH_2)_2 + H_2O.$$

The ammonium salt, $NH_2—NH—CO—O—NH_4$, behaves "normally", and gives an incomplete conversion into semicarbazide. The following data were obtained on samples weighing about 2 grams.

TABLE LIII. *Effect of Temperature and Duration of Heating on Semicarbazide.*

Temperature °C.	Duration of Heating Hours	Yield of $NH_2—NH—CO—NH_2$ Percent
110	20	36.6
120	20	51.2
120	40	51.4
130	20	43.4
145	20	21.7

AMMONIUM SALTS OF DIBASIC ACIDS.

Ammonium oxalate that has been heated at 100° until freed of its water of crystallization enters upon a complex decomposition at higher temperatures. Some oxamide [165] is formed, and ammonia, carbon

[163] Fichter and Becker, *ibid.* p. 3483.
[164] Stollé and Hofmann, *Ber.* 37, 4523 (1904); Fichter and Becker, *Ber.* 44, 3483 (1911).
[165] Dehn and Heuse, *J. Am. Chem. Soc.* 29, 1137 (1907).

monoxide, carbon dioxide, cyanogen and hydrogen cyanide are evolved. Calcagni observed that ammonium oxalate[166] liberates water and ammonia at 120°; at 195° the temperature remains constant while oxides of carbon are abundantly evolved. There is some sublimate of white, pure ammonium carbonate, and a black residue which is largely oxamic acid, $HO_2C—CONH_2$. Oxamic acid is also formed by the direct heating of acid ammonium oxalate (Dehn and Heuse).

The hydrazine oxalates,[167] both $(N_2H_5)_2C_2O_4$ and $N_2H_5.HC_2O_4$, decompose into a variety of products: water, ammonia, hydrogen cyanide, hydrazine, carbon dioxide, carbon monoxide, nitrogen and free carbon.

The conversion of *ammonium succinate* into *succinimide* by distillation is a typical example of a number of ring closures which may be effected by heating[168] diammonium salts, or ammonium acid salts.

$$\begin{matrix} CH_2—CO_2NH_4 \\ | \\ CH_2—CO_2NH_4 \end{matrix} \longrightarrow \begin{matrix} CH_2—CO \\ | \\ CH_2—CO \end{matrix} >NH + 2H_2O + NH_3$$

or,

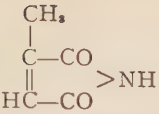
$$\begin{matrix} CH_2—CO—OH \\ | \\ CH_2—CO_2NH_4 \end{matrix} \longrightarrow \begin{matrix} CH_2—CO \\ | \\ CH_2—CO \end{matrix} >NH + 2H_2O$$

One hundred grams of succinic acid,[169] converted into the ammonium salt and heated, gives 65 grams of pure succinimide. A convenient way to prepare succinimide is to distil a mixture of one mol of potassium succinate and two mols of ammonium chloride.

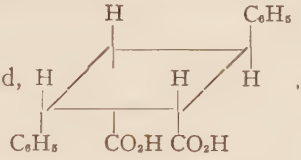
*Iso*propyl succinimide, $\begin{matrix} (CH_3)_2CH—CH—CO \\ | \\ CH_2—CO \end{matrix} >NH$, is formed[170] by heating ammonium *iso*propylsuccinate in a current of ammonia.

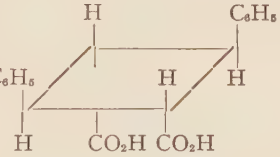
Glutarimide,[171] $(CH_2)_3<\begin{matrix} CO \\ CO \end{matrix}>NH$; glutaric ethyl imide, $(CH_2)_3<\begin{matrix} CO \\ CO \end{matrix}>NC_2H_5$; and glutimide,[172] $H_2N—C_5H_6<\begin{matrix} CO \\ CO \end{matrix}>NH$, all are formed by heating to 170-190° the corresponding ammonium or ethylammonium salts. When ammonium hydrogen citraconate[173] is heated at 180°, there is formed

[166] Calcagni, *Gazz. chim. ital.* **50**, I, 245 (1920).
[167] Turrentine, *J. Am. Chem. Soc.* **32**, 577 (1910).
[168] Fehling, *Ann.* **49**, 196 (1844).
[169] Menschutkin, *Ann.* **162**, 166 (1872).
[170] Roser, *Ann.* **220**, 276 (1883).
[171] Bernheimer, *Gazz. chim. ital.* **12**, 281 (1882).
[172] Habermann, *Ann.* **179**, 251 (1875).
[173] Gottlieb, *Ann.* **77**, 274 (1851).

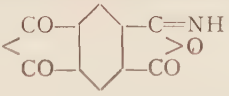
citraconic imide,  . Camphoric imide is similarly formed [174] from the acid ammonium salt at 150-160°, and the corresponding ethyl imide, $C_{10}H_{14}O_2{=}N{-}C_2H_5$, as well,[175] by dry-distillation methods.

A reaction featuring two types of dehydration is the conversion of ethylammonium acid malate [176] into ethyl-fumarimide, $C_4H_2O_2{=}N{-}C_2H_5$. The *N*-methyl analog,[177] methyl-fumarimide, has been prepared also in this manner. Both reactions proceed below 200°.

The best way to prepare γ-truxillimide [178] is to heat the ammonium salt of γ-truxillic-acid,  , a dimer of cinnamic acid.

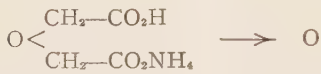
The diammonium salt of ε-truxillic acid,  , however, only gives small yields of its imide [179] by dry distillation. Chiefly, it changes into the diamide, with lesser amounts of the amidic acid.

Although phthalimide is usually made from phthalic anhydride and ammonia, it may be prepared [180] by heating ammonium acid phthalate.

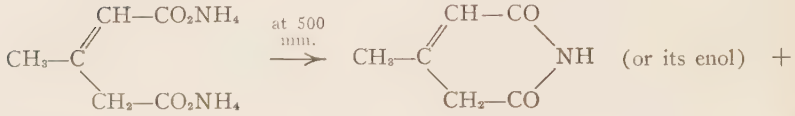
Pyromellitic imide, , is formed [181] by heating ammonium pyromellitate at 200°. This imide, if heated in a vacuum at 300° (or by long heating in high boiling solvents), undergoes rearrangement into the labile form of the asymmetric imide,  . The stable form, , is produced by heating ammonium mellitate in lots of 5 grams for 6-10 hours.

[174] Laurent, *Ann.* **60**, 329 (1846); Ballo, *Ann.* **197**, 331 (1879) obtained the imide similarly from ammonium camphoramate.
[175] Wallach and Kamenski, *Ann.* **214**, 247 (1882).
[176] Piutti, *Gazz. chim. ital.* **18**, 483 (1888).
[177] Giustiniani, *ibid.* **22**, I, 170 (1892).
[178] Stoermer and Fretwurst, *Ber.* **58**, 2718 (1925).
[179] Stoermer, Neumaerker and Schmidt, *Ber.* **58**, 2707 (1925).
[180] Laurent, *Ann.* **41**, 110 (1842).
[181] Meyer and Steiner, *Monatsh.* **35**, 391 (1914).

The following cases also give cyclic imides by distillation:



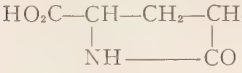
Ammonium acid diglycollate [182]



Ammonium salt of cis-β-methylglutaconic acid [183] *4-methyl-2,6-dihydroxy-pyridine*

Similarly, the ammonium salt of α,β-dimethylglutaconic acid is transformed into 4,5-dimethyl-2,6-dihydroxypyridine, by distilling at 500 mm. Ammonium salt of ioniregentricarboxylic acid [184] is decomposed by dry distillation in a stream of carbon dioxide:

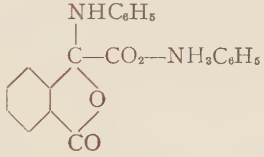
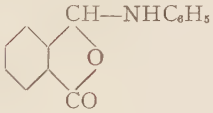
In the last case, the two *meta* carboxyl groups do not participate in the ring closure, but instead the ring closure involves two *ortho* atoms in the nucleus, a fact which has been emphasized repeatedly.

The diammonium salt of glutamic acid changes [185] into the monoammonium salt at 105-115°; the latter yields pyroglutamic acid,  , when heated at 160° for 5 hours. In other words, the decomposition is very much like that of glutamic acid (p. 472).

These reactions show that succinic acid and its ammonium salt follow different pyrolytic courses. Likewise, acids related to glutaric acid change into the anhydride, whereas the ammonium salts yield the imide. Only in the case of glutamic acid may one find a similarity. Another case in which a polybasic acid and its ammonium salt pursue parallel courses is pentane-α,γ,ε-tricarboxylic acid, $HO_2C—CH(CH_2—CH_2—CO_2H)_2$; see p. 419. This is an acid which is related to glutaric and to pimelic acid, but only the pimelic carboxyls appear to participate in the pyrolysis.[186] If the acid is dissolved in an excess of ammonium hydroxide, and the whole evaporated to a semi-solid mass after which it is heated to 150° at atmospheric pressure, ammonia and steam escape.

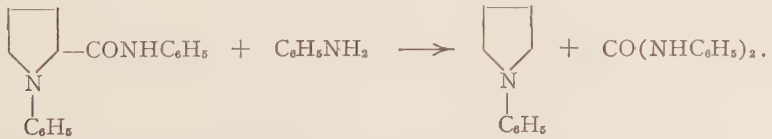
[182] Heintz, *Ann.* **128**, 134 (1863); Würtz, *Ann. chim.* [3] **69**, 349 (1863).
[183] Rogerson and Thorpe, *J. Chem. Soc.* **87**, 1692, 1698 (1905).
[184] Tiemann and Krüger, *Ber.* **26**, 2686 (1893).
[185] Skola, *Z. Zuckerind cechoslav. Rep.* **44**, 347 (1920); *Chem. Abstracts* **15**, 525 (1920).
[186] Perkin, Jr., *J. Chem. Soc.* **85**, 426 (1904).

If now, it is heated at 20 mm. pressure, the mass solidifies completely, then remelts and decomposes with the evolution of much gas and an oily distillate. From the latter may be isolated δ-ketohexahydrobenzoic acid, $HO_2C—CH(C_4H_8)CO$. Three grams of the semicarbazone of the latter is produced from 14 grams of the original acid. The other products were not investigated. This yield, although inferior to that from the free acid anhydride, suffices to show the similarity of the two cases. Whether this condition is generally true with derivatives of pimelic acid cannot be stated.

Fuson [187] has shown that the structure of the aniline derivative of phthalonic acid is  . When heated for a short time in perfectly dry xylene, it gives a practically quantitative yield of *o*-carboxybenzylidene aniline,  . Aniline and carbon dioxide are also formed. This decomposition is entirely inhibited by 0.4 percent of water in the xylene, even after hours of boiling.

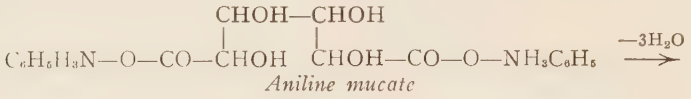
Although its presence was earlier recognized in coal tar, etc., pyrrole was first synthesized by heating *ammonium mucate*. This reaction has rather general application [188] in the formation of *N*-alkyl- or *N*-aryl-pyrroles from alkyl or aryl ammonium salts of mucic acid. Distillation of aniline mucate, for example,[189] gives fairly good yields of *N*-phenyl pyrrole. In this connection, it may be stated that if *N*-phenyl-pyrrole is passed through a tube heated to dull redness, about one-third of it is isomerized into α-phenyl-pyrrole (Pictet and Crépieux).

Considerable amounts of symmetrical diphenylurea accompany the formation of *N*-phenyl-pyrrole in the above preparation. To explain this, Feist [190] assumed the formation of aniline and pyrrole monocarbanilide, and an interaction of these substances:

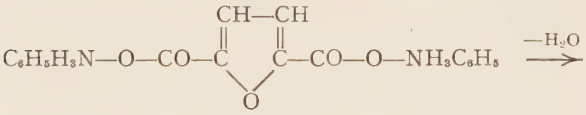


[187] Fuson, *J. Am. Chem. Soc.* **48**, 1094 (1926).
[188] Schwanert, *Ann.* **116**, 270, 278 (1860).
[189] Köttnitz, *J. prakt. Chem.* [2] **6**, 143 (1873); Pictet and Crépieux, *Ber.* **28**, 1905 (1895); Plancher and Ghigi, *atti. chim. ital.* **55**, 757 (1925).
[190] Feist, *Ber.* **35**, 1654 footnote (1902).

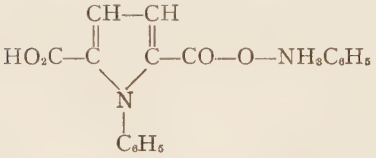
By working at lower temperatures (240°), Pictet and Steinmann[191] were able to confirm this and also were able to supply the remaining steps in the decomposition which precede it. At this temperature, only traces of *N*-phenyl-pyrrole are formed. The steps are as follows:



Aniline mucate

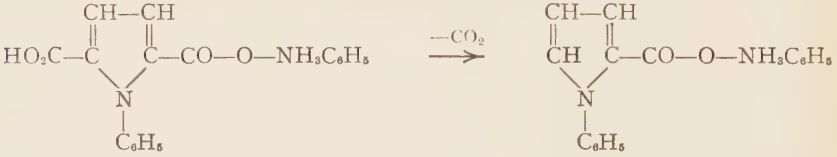


Aniline salt of dehydromucic acid



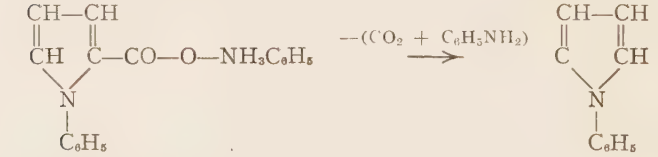
Aniline salt of phenylpyrrole dicarboxylic acid

The aniline salt of phenylpyrrole-dicarboxylic acid, is one of the major products of the reaction. It, however, suffers further pyrolysis:



Aniline salt of phenyl-pyrrole-dicarboxylic acid

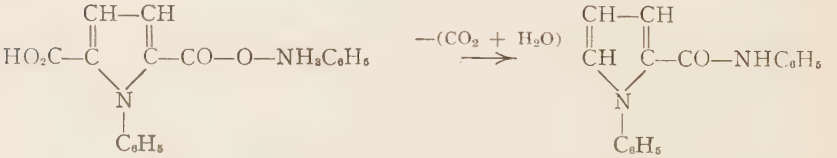
Aniline salt of phenylpyrrole-monocarboxylic acid



Aniline salt of phenylpyrrole-monocarboxylic acid

Phenylpyrrole

and



Aniline salt of phenyl-pyrrole-dicarboxylic acid

Anilide of phenylpyrrole-monocarboxylic acid

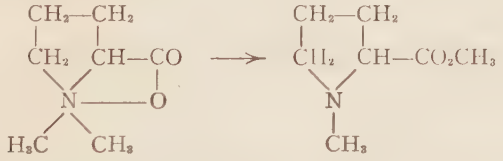
[191] Pictet and Steinmann, *Ber.* **35**, 2532 (1902).

In this pyrolysis, the chief reaction products are the aniline salts of phenylpyrrole-mono- and di-carboxylic acids, and the anilide of phenylpyrrole-monocarboxylic acid. At higher temperatures, these compounds interact with the formation of phenylpyrrole, aniline, diphenylurea and carbon dioxide. In this connection, it is interesting to learn that potassium furoate may be formed by heating [192] the acid potassium salt of mucic acid to 150-180°.

Pasteur's discovery [193] of mesotartaric acid resulted from heating the cinchonine salt of *d*-tartaric acid at 170°. Racemic acid, or rather its cinchonine salt, is also produced. Tartaric acid itself would have decomposed at this temperature. Therefore, the cinchonine imparts stability to the molecule. The aniline salt of phenylpyrrole-dicarboxylic acid is likewise more stable than the free acid, since the latter is decomposed [191] into phenylpyrrole at 235-240°, whereas the former may be synthesized in fairly good yields from aniline mucate at 240°.

Betaine, of interest because it occurs in large amounts [194] in the molasses from beet-root sugar, may be formed from methyl dimethylaminoacetate by 8 hours' heating at 200° in a sealed tube. The reverse action [195] occurs by distilling betaine at 300°:

In both processes the yields are good (about 85 percent and 65 percent respectively). The rearrangement of the α-betaines to the esters is a general reaction, but the reverse process, namely, the preparation of the betaines from the esters, is not. The betaine-like substance, stachydrin, changes by distillation [196] into the isomeric ester. This occurs even at the melting point, 235°.

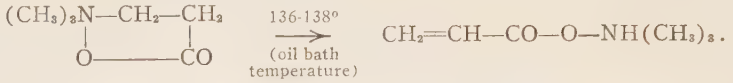


Some trimethylamine is also formed as a further decomposition product.

β-Betaines are less stable than the α- or γ-betaines. In the simple cases, they rearrange into a salt of acrylic acid when heated. β-Tri-

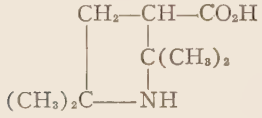
[192] Schmitt and Cobenzl, *Ber.* **17**, 600 (1884).
[193] Pasteur, *Compt. rend.* **37**, 164 (1853).
[194] Stoltzenberg, *Ber.* **45**, 2248 (1912).
[195] Willstätter, *Ber.* **35**, 584, 597, 604 (1902).
[196] Schulze and Trier, *Ber.* **42**, 4657 (1909).

methylpropiobetaine, for example, is thermally decomposed[197] into trimethylammonium acrylate:

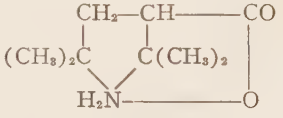


The β-amino acids (p. 468) were observed to undergo an identical type of change. If the inner salt structure is adopted for the β-amino acids, the similarity is apparent. Thus:

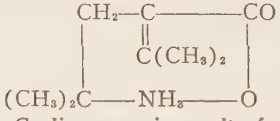
2,2,5,5-Tetramethylpyrrolidone-3-carboxylic acid reacts in accordance



2,2,5,5-Tetramethyl-pyrrolidone-3-carboxylic acid

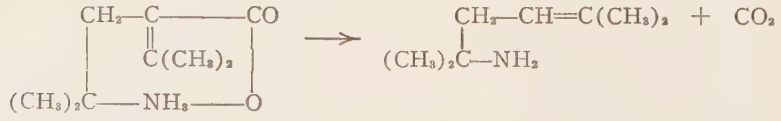


Inner salt of 2,2,5,5-tetramethyl-pyrrolidone-3-carboxylic acid

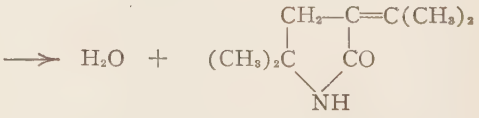


Cyclic ammonium salt of α-isopropylidene-γ-methyl-γ-amino-valeric acid

with its inner-salt formula. Were it to decompose in the above manner, since it is in reality a β-amino acid, the cyclic ammonium salt, which is a γ-amino acid, would be anticipated. This, apparently, is unstable, and undergoes pyrolysis[198] in two ways to produce the substances which are actually isolated:



and also,



[197] Willstätter, *Ber.* **35**, 612 (1902).
[198] Pauly and Rossbach, *Ber.* **32**, 2008 (1899); Pauly and Hültenschmidt, *Ber.* **36**, 3351 (1903).

The latter reaction is the customary lactam formation of a γ-amino acid, and the former is a decarboxylation of an α,β-unsaturated acid.

γ-Betaines, such as γ-trimethyl-butyrobetaine, decompose by heating [199] into γ-lactones and a tertiary amine:

This is quite in contrast to the behavior of γ-amino acids, which form γ-lactams by the elimination of water. δ-Trimethyl-valerobetaine [200] resembles the α- and the γ-betaines in its pyrolysis. It melts with decomposition, rearranging in part into methyl δ-dimethylaminovalerate, and decomposing in part into trimethylamine and valerolactone.

[199] Willstätter, *Ber.* **35**, 594 (1902).
[200] Willstätter and Kahn, *Ber.* **37**, 1857 (1904).

CHAPTER 17.

ESTERS.

Esters of Simple Aliphatic Acids.

Formates.

Among the esters, formates are unique in possessing the functional group of aldehydes. It is of interest, therefore, to ascertain whether or not formates decompose like aldehydes, in which case a primary product of the reaction would be carbon monoxide:

Aldehydes:

$$H—CO—R \longrightarrow CO + RH$$

Formates:

$$H—CO—OR \longrightarrow ?$$

The results indicate that formates behave differently from aldehydes.

When methyl formate[1] is passed rapidly through a short platinum tube (2 × 110 mm.), heated to 1150°, the results are best explained on the assumption that the initial pyrolysis yields two mols of formaldehyde:

$$H—CO—OCH_3 \longrightarrow 2HCHO.$$

Carbon monoxide and hydrogen constitute about 96 percent of the gaseous products. These gases are regarded as decomposition products of the formaldehyde:

$$HCHO \longrightarrow H_2 + CO.$$

A limited quantity of methanol is formed, which is probably synthesized by the interaction of formaldehyde and hydrogen. In one run, 1.535 grams of methyl formate formed 0.013 gram of liquid formaldehyde, 0.34 gram of dissolved formaldehyde and 1103 cc. of gas. Analysis of the gas, by volume, is: carbon monoxide, 53.0 percent; hydrogen, 43.1 percent; methane, 1.5 percent; carbon dioxide, 1.8 percent; formaldehyde, 0.6 percent. The pyrolysis of methyl formate was cited to illustrate the rule of "least molecular deformation" (p. 11). Its mode of pyrolysis differs very materially from that of its isomer, acetic acid, but is quite similar to that of its homolog, methyl acetate.

Much the same type of pyrolysis[2] is apparent in the case of tri-

[1] Muller and Peytral, *Compt. rend.* **179**, 831 (1924); Peytral, *Bull. soc. chim.* **37**, 562 (1925)
[2] Hentzschel, *J. prakt. Chem.* [2] **36**, 99, 305 (1887); Grignard, Rivat and Urbain, *Compt. rend.* 169, 1074 (1919); Kling and others, *ibid.* **169**, 1166 (1919).

chloromethyl chlorocarbonate. Even ten degrees below its boiling point (127°), there is a slight dissociation into phosgene:

$$Cl—CO—O—CCl_3 \longrightarrow 2COCl_2.$$

At higher temperatures this becomes more pronounced. The ethyl ester, $Cl—CO—O—C_2H_5$, is stable at 200°.

Ethyl formate starts to decompose [3] at 300°. From 10 cc. of ester, in one experiment 400 cc. of gas was collected, with the following composition: 45.1 percent hydrogen, 29.5 percent carbon monoxide, 18.2 percent carbon dioxide, 7.2 percent ethylene. Subsequently, it will be shown that esters that possess the general formula, $R—CO—O—CH_2—CH_2—R'$, may be expected to decompose into free acid and olefine, $R—CO_2H$ and $CH_2=CHR'$. Viewed from this angle, ethyl formate should yield formic acid, or its decomposition products, and ethylene. Since formic acid may pyrolyze either into $CO + H_2O$ or into $CO_2 + H_2$ at this temperature, this affords a qualitative explanation for the substances isolated. Engler believed that the low value for ethylene was due to "polymerized ethylene" in the residue. Furthermore, he asserted that the reaction,

$$CO + H_2O \longrightarrow CO_2 + H_2,$$

vitiated the results. However, Hinshelwood (p. 332) has demonstrated that even at 350°, carbon monoxide and water do not react.

Above 300°, amyl formate yields gases which appear to indicate an initial decomposition into amylene and formic acid. One hundred parts of the gases yield 44.3 parts of hydrogen, 23.2 of carbon monoxide, 16.7 of carbon dioxide and 15.8 of amylene.

It is stated [4] that cholestane, $C_{27}H_{48}$, may be formed by heating dihydrocholesteryl formate, $C_{27}H_{47}—O—COH$, at 290° and 100 mm. Similarly myricyl formate, $C_{30}H_{61}—O—COH$, yields triacontane, $C_{30}H_{62}$. It would seem more reasonable for the unsaturated compounds, $C_{27}H_{46}$ and $C_{30}H_{60}$, to be formed instead.

One of the best synthetic methods [5] for allyl alcohol is essentially a thermal decomposition of glyceryl formate.

$$H—CO—O—C_3H_5(OH)_2 \longrightarrow C_3H_5OH + CO_2 + H_2O.$$

In practice, a mixture of formic acid of 85 percent strength (0.4 mol) and glycerol (1 mol) is rapidly heated to 195°. During this period, carbon dioxide is evolved and some liquid distils, which is disregarded. Between 195-260° (thermometer in liquid), the crude allyl alcohol is

[3] Engler and Grimm, *Ber.* **30**, 2922 (1897).
[4] German patent 296,741 (1917); *Chem. Abstracts* **13**, 325 (1919).
[5] "Organic Syntheses," Vol. I, New York, John Wiley and Sons, 1921, p. 15.

formed and distils away. Another 0.3 mol of formic acid is added to the residue, and the distillation to 260° is repeated. This is again repeated with a final 0.3 mol, making a total of 1 mol of acid. From the distillate (195-260°) a 34 percent yield of allyl alcohol is isolable. (For glyceryl oxalates, see page 547.)

Much the same procedure may be employed in the synthesis of homologs of allyl alcohol. Distillation at 270° of a mixture of the mono- and di-formates of ethylglycerol [6] yields a mixture of vinyl ethyl carbinol, $CH_2{=}CH{-}CHOH{-}C_2H_5$, and γ-ethylallyl alcohol, $C_2H_5{-}CH{=}CH{-}CH_2OH$. From the diformate [7] of the structure,

$$\begin{array}{l} CH_2\text{———}CH\text{———}CH{-}C_2H_5 \\ |\quad\quad\quad |\quad\quad\quad | \\ O{-}CO{-}H\quad O{-}CO{-}H\quad OH \end{array}$$

, one obtains carbon dioxide, water and γ-ethylallyl formate, $\begin{array}{l} CH_2{-}CH{=}CH{-}C_2H_5 \\ | \\ O{-}CO{-}H \end{array}$, exclusively on heating.

This reaction permits an interesting synthesis of γ-ethylallyl alcohol in 20 percent yields from vinyl ethyl carbinol:

$$CH_2{=}CH{-}CHOH{-}C_2H_5 \xrightarrow{Br_2} CH_2Br{-}CHBr{-}CHOH{-}C_2H_5 \xrightarrow{2H-CO_2Na}$$

$$\begin{array}{l} CH_2\text{———}CH\text{———}CH{-}C_2H_5 \\ |\quad\quad\quad |\quad\quad\quad | \\ O{-}CO{-}H\quad O{-}CO{-}H\quad OH \end{array} \xrightarrow{heat} \begin{array}{l} CH_2{-}CH{=}CH{-}C_2H_5 \\ | \\ O{-}CO{-}H \end{array} \xrightarrow{hydrolysis}$$

$$HOCH_2{-}CH{=}CH{-}C_2H_5$$

In brief, this type of pyrolysis is a convenient indirect method of transformation from a glycol grouping to an olefine configuration;

$$-CHOH{-}CHOH \longrightarrow -CH{=}CH-.$$

An additional example is the decomposition of the mono- and di-formates of dimethyl glycerol into pentene-3-ol-2. Since this decomposition [8] occurs at 200°, and since the tri-formate is stable at 200°, this indicates the greater instability of the former. The formates of methyl-ethyl glycerol also emphasize this point. The mono-formate undergoes pyrolysis at 220° into hexene-2-ol-4. At the same temperature, the di-formate yields hexene-3-ol-2, and the tri-formate is stable. Thus,

$$\begin{array}{l} -CH\text{———}CH- \\ |\quad\quad\quad | \\ OCOH\quad OCOH \end{array}$$ is more stable than $\begin{array}{l} -CH{-}CHOH- \\ | \\ OCOH \end{array}$.

Cases exist, however, in which the decomposition of a glycol di-formate occurs with ease. One such is the diformate of divinylglycol [9] which breaks down between 165-200°:

[6] Delaby, *Compt. rend.* **176**, 1898 (1923); *Ann. chim.* **20**, 196 (1923).
[7] Delaby, *Compt. rend.* **181**, 722 (1925).
[8] Delaby and Morel, *Bull. soc. chim.* **39**, 416 (1926).
[9] van Romburgh and van Dorssen, *J. Chem. Soc.* **90**, 130, 722 (1906).

$$\begin{matrix} CH_2{=}CH{-}CH{-}O{-}COH \\ | \\ CH_2{=}CH{-}CH{-}O{-}COH \end{matrix} \longrightarrow \begin{matrix} CH_2{=}CH{-}CH \\ \| \\ CH_2{=}CH{-}CH \end{matrix} + CO + CO_2 + H_2O.$$

Hexatriene is similarly formed when a mixture of the diformate and the original glycol is distilled. One would suspect a better yield in this case.

Not only the glycols and glycerols, but the higher polyhydroxy alcohols as well, yield unsaturated compounds when their formates are subjected to distillation. Erythritol diformate, for example,[10] yields butadiene and also crotonaldehyde, dihydrofurfuran and the monoformate of crotonylene glycol. The following equations express this relationship:

$$\begin{aligned} (HO)_2C_4H_6(OCOH)_2 &\longrightarrow CO_2 + H_2O + HO{-}C_4H_6{-}OCOH \\ &\longrightarrow 2CO_2 + 2H_2O + CH_2{=}CH{-}CH{=}CH_2 \\ &\longrightarrow CO_2 + CO + 2H_2O + C_4H_6O \end{aligned}$$

The C_4H_6O represents not only $CH_3{-}CH{=}CH{-}CHO$ but also $\begin{matrix} CH{=}CH \\ | \quad\quad | \\ CH_2 \quad CH_2 \\ \diagdown \quad \diagup \\ O \end{matrix}$. By analogy with experiments such as the above, von Romburgh attempted to synthesize spiropentane,[11] $\begin{matrix} CH_2 \quad\quad CH_2 \\ | \quad > C < | \\ CH_2 \quad\quad CH_2 \end{matrix}$, by heating pentaerythritol tetraformate, $C(CH_2O_2CH)_4$. However, at 220-230° it evolves carbon monoxide quantitatively, and leaves a residue of pure erythritol. It will be noticed that this is a 1,3-glycol. The formates of other 1,3-glycols, such as $\begin{matrix} CH_3{-}CH{-}CH_2{-}CH{-}CH_3 \\ | \quad\quad\quad | \\ OH \quad\quad\quad OH \end{matrix}$ and $CH_2(CH_2OH)_2$, are more resistant towards heat.

Mannitan and *iso*mannide, both dehydration products of mannitol, are formed when mannitol interacts with formic acid. The diformate of mannitan ($C_6H_{12}O_5$) begins to decompose [12] with a lively evolution of gases at 210°, giving two concurrent reactions: [13]

$$C_6H_{10}O_3(OCHO)_2 \begin{cases} \nearrow CO + CO_2 + C_6H_{12}O_4 \\ \searrow 2H_2O + 2CO_2 + \begin{matrix} CH{-}CH{=}CH \\ \| \quad\quad | \\ CH{-}O{-}\!-CH{-}CH_3 \end{matrix} \end{cases}$$

methyl-α-pyrane

[10] Henninger, *Compt. rend.* **98**, 149 (1884); *Ann. chim.* [6] **7**, 217 (1886).
[11] van Romburgh, *Z. physik. Chem.* **130**, 334 (1927).
[12] Fauconnier, *Compt. rend.* **100**, 914 (1885).
[13] Windaus and Tomich, *Nachr. kgl. Ges. Wiss. Göttingen* **1917**, 462; *Chem. Abstracts* 13, 2863 (1919).

ACETATES.

Methyl esters, quite generally, possess a comparatively high stability towards heat. This is also true of other esters such as the benzyl esters which are related to methyl in that they possess no hydrogen atoms on the β-carbon. The limiting temperature at which *methyl acetate* may be heated without decomposing seems not to have been ascertained. Mlle. Peytral [14] has investigated its behavior as it was passed through a short platinum tube at 1100°. There is evidence for two concurrent decompositions:

$$(1)\quad CH_3{-}CO{-}O{-}CH_3 \longrightarrow CH_3{-}CO{-}H + HCHO$$
$$(2)\quad 2CH_3{-}CO_2CH_3 \longrightarrow 2CH_3{-}CO_2H + C_2H_4.$$

By secondary reactions, acetaldehyde pyrolyzes further into carbon monoxide and methane; formaldehyde into carbon monoxide and hydrogen; and acetic acid either into carbon monoxide and methane or into water, ethylene and two molecules of carbon monoxide (from 2 molecules of acetic acid). Twenty percent of the gaseous products are hydrogen, 23 percent methane, and 45 percent carbon monoxide.

Methyl phenylacetate [15] decomposes slowly at 360° in a sealed tube into toluene and methanol. Two-thirds of the gaseous products are reported to be carbon dioxide, and the remainder carbon monoxide and methane. Engler's explanation of this pyrolysis treats it more as a hydrolysis than a pyrolysis. He assumed the presence of enough water to cause hydrolysis of the ester into phenylacetic acid and methanol, whereupon the former would change further into toluene and carbon dioxide. To be sure, phenylacetic acid does gradually change into toluene (p. 336), but a more plausible reaction mechanism is the following, based on the methyl acetate pyrolysis:

$$C_6H_5CH_2{-}CO{-}O{-}CH_3 \longrightarrow [C_6H_5CH_2{-}CHO] + [CH_2O]$$
$$\downarrow \qquad\qquad \downarrow$$
$$C_6H_5CH_3 + CO \qquad H_2 + CO$$

Part of the hydrogen may reduce the formaldehyde to methanol. Concurrently, there may also be the disproportionation into phenylacetic anhydride and dimethyl ether (or their decomposition products), thereby resembling the behavior of benzyl benzoate (see below).

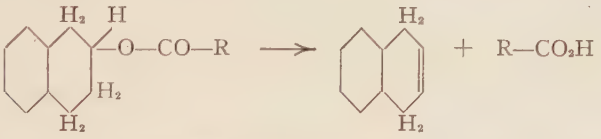
It is interesting to note that much the same mechanism may be used to explain the formation (p. 260) of acetaldehyde following the pyrolysis of acetol acetate [16] at 430-450°:

[14] Peytral, *Bull. soc. chim.* [4] **31**, 121 (1922).
[15] Engler and Low, *Ber.* **26**, 1440 (1893).
[16] Nef, *Ann.* **335**, 263 (1904).

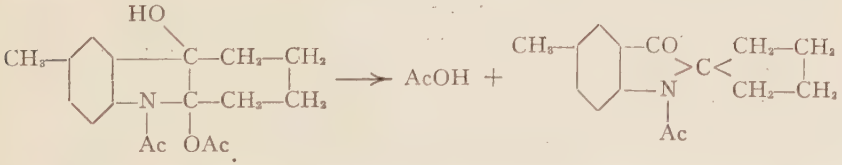
$$CH_3—CO—O—CH_2COCH_3 \longrightarrow CH_3CHO +$$
$$[HCO—CO—CH_3] \longrightarrow CO + CH_3CHO.$$

Ethyl acetate[15] is unchanged after 10 hours' heating at 290°, but it changes smoothly[17] into acetic acid and ethylene by passage through a tube heated to a dark red glow. Tertiary amyl acetate, $CH_3—CO—O—C(C_2H_5)(CH_3)—CH_3$, decomposes into acetic acid and amylene at much lower temperatures.[18] Given sufficient time, this reaction goes practically to completion at 155°. Thus, 4 percent changes in 20 hours; 23 percent in 40 hours; 83 percent in 60 hours; and 96 percent in 92 hours. Menschutkin performed these quantitative experiments with 0.3 gram samples in a sealed tube of about 1 cc. capacity. With a lower temperature, 140°, only 4 percent decomposes in 96 hours. Still lower, at 125°, only 11 percent changes in 46 days, and at 100° the transformation is negligible.

The esters of *ac*-tetrahydro-*β*-naphthol change[19] into dihydronaphthalene by distillation, in accordance with the general scheme for the pyrolysis of simple esters:

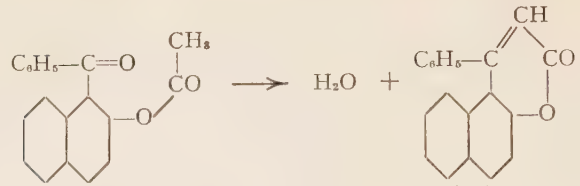


Acetic acid is detached[20] from 9-acetyl-10-acetoxy-11-hydroxy-6-methyl-hexahydrocarbazole by heating it for one minute at 240°. The product which is formed is 6-acetyl-9-methyl-*ψ*-indoxyl*spiro*cyclopentane.



The acetate of 1-benzoyl-2-hydroxynaphthalene[21] has no chance to lose acetic acid by pyrolysis, but instead water is detached with the ring-closure to a derivative of coumarin:

[17] Oppenheim and Precht, *Ber.* **9**, 325 (1876).
[18] Menschutkin, *Ber.* **15**, 2512 (1882).
[19] Bamberger and Lodter, *Ber.* **23**, 209 (1890).
[20] Manjunath and Plant, *J. Chem. Soc.* **1926**, 2263.
[21] Dischendorfer and Danziger, *Monatsh.* **48**, 332 (1927).



β-(α-benzoyl)-naphthyl acetate *4-phenyl-5,6-benzocoumarin*

The preparation of potassium vinylsulfonate [22] is another case of the formation of an acid, acetic acid, by heating an ester:

$$CH_3—CO_2—CH_2CH_2SO_3K \longrightarrow CH_3CO_2H + CH_2=CH—SO_3K.$$

potassium acetyl-isethionate — *potassium vinylsulfonate*

Triphenylmethyl acetate,[23] $CH_3—CO—O—C(C_6H_5)_3$, and also the benzoate, change into triphenylmethane when heated. These decompositions are probably complex. A detailed account of these experiments has not as yet been published, but it would be interesting to learn if 9-phenyl fluorene and acetic acid are formed. These substances would be anticipated if the reaction followed a parallel course to that of triphenylchloromethane (see p. 138). This is a reasonable assumption, since triphenylmethyl chloride is also an ester.

The polymerization [24] of vinyl acetate, $CH_3—CO—O—CH=CH_2$, is initiated by heating under a reflux. After a time, this is withdrawn and a new cold portion added. The polymerization is completed in another vessel.

Esters of Other Simple Aliphatic Acids.

Since the equation for the pyrolysis of the higher aliphatic esters indicates the formation of acid and olefine:

$$R—CO_2—CH_2—CH_2R' \longrightarrow R—CO_2H + CH_2=CHR',$$

it is not surprising that this method has been much used for the preparation of α-unsaturated hydrocarbons. Krafft [25] was a pioneer in this work.

Heintz had earlier demonstrated [26] that cetyl palmitate yields palmitic acid and hexadecene when heated:

$$C_{15}H_{31}—CO_2—C_{16}H_{33} \longrightarrow C_{15}H_{31}—CO_2H + C_{16}H_{32}.$$

Krafft showed that many of the secondary decompositions are avoidable if the heating is performed under diminished pressure (300-

[22] Kohler, *Am. Chem. J.* **19**, 728 (1897); **20**, 680 (1898).
[23] Norris and Young, *J. Am. Chem. Soc.* **46**, 2581 (1924).
[24] Brit. Pat. 261,406 Nov. 14, 1925; *Chem. Abstracts* **21**, 3369 (1927).
[25] Krafft, *Ber.* **16**, 3018 (1883); **19**, 2227 (1886).
[26] Heintz, *Pogg. Ann.* **93**, 536 (1854).

400 mm.). The residue in the retort is negligible. He identified the hexadecene as $CH_2{=}CH{-}(CH_2)_{13}{-}CH_3$. With this method, Gault and Altchidjian [27] obtained a 25 percent yield of purified hexadecene.

Similarly (Krafft), octadecyl palmitate undergoes pyrolysis by distillation at 120-140 mm. into palmitic acid and octadecene, $C_{16}H_{33}{-}CH{=}CH_2$; tetradecyl palmitate at 500 mm. into tetradecene, $C_{14}H_{28}$; and dodecyl palmitate into the olefine, $C_{12}H_{24}$. Dodecyl palmitate distils in a low vacuum, so that a pressure of 600 mm. is required. Care must be taken at higher pressures to avoid the formation of palmitone from the palmitic acid. Ethyl stearate decomposes slowly [28] in a sealed tube at 300° into stearic acid and ethylene.

Sixty percent yields each of styrene and phenylacetic acid result when phenylethyl phenylacetate [29] is maintained for 11 hours in a distilling flask at 320°, a temperature just below its boiling point:

$$C_6H_5CH_2{-}CO_2{-}CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2{-}CO_2H + CH_2{=}CH{-}C_6H_5.$$

Only a small amount of brown residue fails to distil.

Stearyl glycide,[30] $C_{17}H_{35}{-}CO{-}O{-}CH_2{-}CH(O){-}CH_2$, boils at 161° with partial decomposition into acrolein. Levene and Walti [30a] report that glycidol acetate, $CH_3CO_2{-}CH_2{-}CH(O){-}CH_2$, gives "polymers" by heating for five days at 132-145°. These polymers may have arisen from acrolein. Distillation of cholesteryl oleate at 13 mm. gives a 50 percent yield of α-cholesterilene.[31] The esters of camphylcarbinol, $C_8H_{14}{<}^{CH{-}CH_2OH}_{CO}$, with the C_1 to C_3 acids undergo considerable decomposition by distillation [32] in an ordinary vacuum into the acid and methylene camphor, $C_8H_{14}{<}^{C{=}CH_2}_{CO}$, although these esters may be distilled in the vacuum of a mercury pump (temperatures, 60° to 150°). The hexahydrobenzoate, phenylacetate, hydrocinnamate, sorbate and crotonate all behaved similarly.

Ethyl crotonate and ethyl malonate are decomposed [33] by a white

[27] Gault and Altchidjian, *Ann. chim.* [10] **2**, 217 (1924).
[28] Colson, *Compt. rend.* **147**, 1054 (1908).
[29] Hibbert and Burt, *J. Am. Chem. Soc.* **47**, 2243 (1925).
[30] Grün and Limpacher, *Ber.* **59**, 694 (1926).
[30a] Levene and Walti, *J. Biol. Chem.* **79**, 368 (1928).
[31] Fischer and Treibs, *Ann.* **446**, 241 (1925).
[32] Rupe and Schaerer, *Helv. Chim. Acta* **8**, 853 (1925).
[33] Wilsmore and Stewart, *Proc. Chem. Soc.* **23**, 309 (1908).

hot platinum wire into ethylene and crotonic or malonic acids, the latter pyrolyzing further into methane and carbon dioxide.

Phenyl Esters of the Higher Aliphatic Acids.

These have been studied and are of interest because the phenyl group cannot be severed as an unsaturated hydrocarbon. Therefore, the decomposition would be expected in another part of the molecule. Phenyl stearate [34] and phenyl palmitate, when heated at 300-320° in a nitrogen-filled bomb, yield pentadecane and tridecane respectively. This indicates that phenyl acrylate is the other product; instead, however, acetylene and phenyl formate (and some phenol) are actually formed. Since phenyl acrylate changes into phenol, carbon monoxide and acetylene in a sealed tube at 320°, the mechanism seems established. Thus:

$$R{-}CH_2{-}CH_2{-}CO_2C_6H_5 \longrightarrow R{-}H + [CH_2{=}CH{-}CO_2C_6H_5]$$

$$\downarrow$$

$$H{-}C{\equiv}C{-}H + H{-}CO_2C_6H_5$$

$$\downarrow$$

$$CO + C_6H_5OH.$$

Similarly, phenyl laurate gives rise to phenol at 300-320°. Curiously, when phenyl stearate is heated at 320° and atmospheric pressure, no acetylene or ethylene are evolved, and the residue in the flask contains no paraffin. Phenol and carbon monoxide are produced, however.

The fact that phenyl acrylate pyrolyzes as indicated into acetylene, carbon monoxide and phenol raises the question as to the behavior of the homologs and aromatic analogs, $R{-}CH{=}CH{-}CO_2C_6H_5$, towards heat. With a parallel reaction mechanism, this should provide a neat method of synthesis of the higher acetylenes. Apparently, however, this is not the course taken. Anschütz [35] showed that slow distillation of phenyl cinnamate at atmospheric pressure produces carbon dioxide and stilbene:

$$C_6H_5CH{=}CH{-}CO_2C_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + CO_2.$$

This appears to be a general reaction:

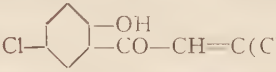
$$C_6H_5CH{=}CH{-}CO_2Ar \longrightarrow C_6H_5CH{=}CHAr + CO_2,$$

since it is also found to hold [36] when Ar represents *p*-cresyl, *β*-naphthyl, *p*-chlorophenyl and *p*-bromophenyl. This subject has also been investigated by Skraup and Beng, who reported [37] stilbene and about two-

[34] Skraup and Nieten, *Ber.* **57**, 1294 (1924).
[35] Anschütz, *Ber.* **18**, 1945 (1885).
[36] Anschütz, *Ber.* **60**, 1320 (1927).
[37] Skraup and Beng, *Ber.* **60**, 942 (1927).

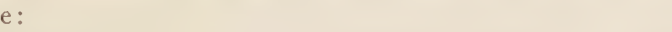
thirds of the calculated quantity of carbon dioxide, and almost no carbon monoxide or phenyl acetylene, from the pyrolysis of phenyl cinnamate. The decomposition temperature is 290-300°, and the yield of pure stilbene is 27 percent (or 58 percent crude). 4-Chloro-stilbene, $Cl—C_6H_4—CH=CHC_6H_5$, may be prepared by heating either $ClC_6H_4—CH=CH—CO_2C_6H_5$ or $C_6H_5CH=CH—CO_2C_6H_4Cl$. The respective temperatures of decomposition are 260-270° and 320-330°, and the yields 23 and 22 percent respectively (or 44 and 47 percent respectively, crude).

A still different type of pyrolysis is encountered in the aryl esters of β,β-dimethylacrylic acid. In these cases, there is rearrangement (Skraup and Beng) to an *o*-hydroxy-ketone:

The yield is only 7 percent at 320-330° if the pure ester is used, but a trace of hydrogen bromide assists the reaction materially giving a 17-25 percent yield at 220-230°. The *p*-chlorophenyl ester behaves analogously and gives rise to the phenolic-ketone,  . A strictly similar case is the rearrangement [38] of phenyl cyclohexane-carboxylate into cyclohexyl *o*-hydroxyphenyl ketone by heating in sealed tubes:

Rearrangement [39] of a different type occurs as *pseudo*-phenylacetic ester is heated at 150° in an evacuated tube for 4 hours. The ester of cyclo-heptatriene carboxylic acid is formed:

Staudinger employed pyrogenic methods [40] in the preparation of phenyl ketene acetal. Six grams of the latter was formed by repeated vacuum distillation (12 mm.) of 15 grams of triethyl *ortho*phenyl-acetate:



With distillation at 760 mm., the *ortho* ester yields not only the ketene acetal but also ethyl phenylacetate.

[38] Skraup and Beifuss, *Ber.* **60**, 1070 (1927).
[39] Buchner and Lingg, *Ber.* **31**, 402, 2247 (1898).
[40] Staudinger and Rathsam, *Helv. Chim. Acta* **5**, 645 (1922).

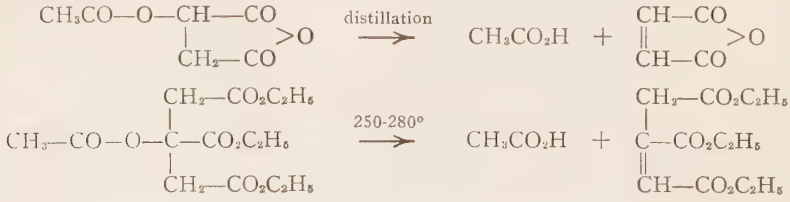
One is accustomed to think of the formation of acetic anhydride in terms of "sodium acetate + acetyl chloride", or of "sodium acetate + chlorides of sulfur or phosphorus", but at present perhaps the cheapest method for its manufacture is from *ethylidene diacetate:*

$$CH_3{-}CH(OCOCH_3)_2 \longrightarrow CH_3CHO + (CH_3CO)_2O.$$

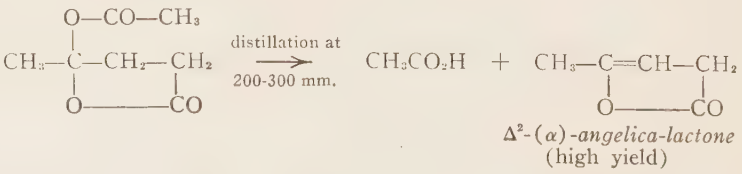
The raw materials for the preparation of this substance are acetylene, air and catalysts. Essentially, its decomposition is one that is a thermal decomposition, but in practice, catalysts (acids, zinc chloride, sulfur dioxide and sulfur trioxide, etc.) are usually inserted to effect the transformation at a fairly low temperature. Geuther [41] reported a partial decomposition at 168°, the boiling point, which became very noticeable on repeated distillations. The following incomplete list [42] of patents bears witness to the recent interest in this development. Catalysts are mentioned in all of them.

More Complex Acetic Esters.

Acetyl malic anhydride, acetyl citric esters [43] and "acetyl levulinic acid",[44] although dissimilar in many respects all possess the common grouping, $CH_3{-}CO{-}O{-}CR_2{-}CH{=}$, and all undergo pyrolysis into acetic acid and the unsaturated structure, $R_2C{=}C{=}$. The following equations make this clear:



(A residue of ethyl aconitate remains after the calculated weight of acetic acid has been eliminated.)



Δ^2-(α)-*angelica-lactone*
(high yield)

[41] Geuther, *Ann.* **106**, 249 (1858).

[42] Fr. Pat. 486,591, Apr. 18, 1918; Brit. Pat. 131,399, June 24, 1918; Can. Pat. 217,576, Apr. 11, 1922; U. S. Pat. 1,429,650, Sept. 19, 1922; Ger. Pat. 346,236; U. S. Pat. 1,579,248 and 1,578,454, Apr. 6 and Mar. 30, 1926; Brit. Pat. 238,825, Oct. 13, 1924. Respectively, these are mentioned in *Chem. Abstracts* **14**, 72 (1920); **14**, 284 (1920); **16**, 1781, 3903 (1922); **17**, 1247 (1923); **20**, 1630, 1995 (1926).

[43] Anschütz and Bennert, *Ann.* **254**, 167 (1889).

[44] Thiele, Tischbein and Lossow, *Ann.* **319**, 184 (1901); Bredt, *Ann.* **256**, 314 (1890).

The presence of the carboxyl group in α-acetoxy acids changes the course of decomposition so that an aldehyde with one less carbon, acetic acid and carbon monoxide are the exclusive products:

$$\mathrm{R{-}\underset{\displaystyle CO_2H}{\underset{|}{CH}}{-}O{-}COCH_3 \longrightarrow R{-}CHO + CO + CH_3CO_2H.}$$

It will be recalled that α-hydroxy acids (p. 426) pyrolyze according to a similar mechanism. α-Acetoxy heptoic acid[45] gives 68.7 percent of capraldehyde. In like fashion,[46] at 250°, α,α′-diacetoxy-sebacic acid, $\mathrm{\underset{\displaystyle OCOCH_3}{\underset{|}{HO_2CCH}(CH_2)_6\underset{\displaystyle OCOCH_3}{\underset{|}{CHCO_2H}}}}$, yields suberic dialdehyde, $\mathrm{HCO{-}(CH_2)_6{-}CHO}$ (see pp. 427 and 442).

In a reaction[47] between acetic anhydride and an α-glycol, trimethyl-2,4,4-pentanediol-1,2 (at 170-180° for 9 hours), the diacetate ester was undoubtedly formed, and the following pyrolytic reaction was given as explanation of the formation of α,γ,γ-trimethyl valeraldehyde:

$$\mathrm{(CH_3)_3C{-}CH_2{-}\underset{\displaystyle CH_2{-}O{-}COCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}O{-}COCH_3}$$

$$\mathrm{(CH_3)_3C{-}CH{=}C(CH_3){-}CH_2OH}$$

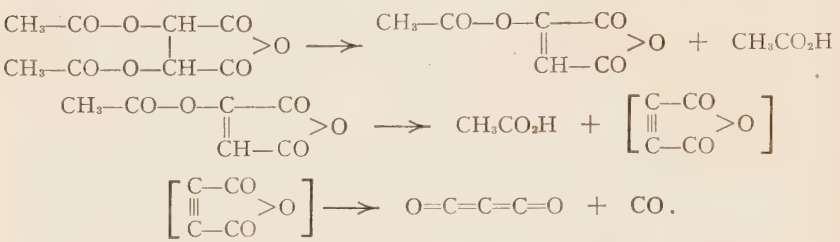
$$\mathrm{(CH_3)_3C{-}CH_2{-}\underset{\displaystyle CHOH}{\underset{\|}{C}}{-}CH_3 \longrightarrow (CH_3)_3C{-}CH_2{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}CH_3.}$$

An extremely interesting case of pyrogenic decomposition is that of *diacetyl tartaric anhydride*.[48] From this compound, one which is very readily prepared from tartaric acid, *carbon suboxide* is obtainable in 41 percent yield (32 grams of the suboxide from an original 250 grams) by distilling its vapors at 11 mm. over a hot platinum filament. This is by far its best method of preparation. The details are given in full in Ott and Schmidt's article, and these have been confirmed by the author. Carbon suboxide is a diketene, O=C=C=C=O. In this connection, it is interesting to recall that ketene, $CH_2{=}C{=}O$, is also best made by pyrogenic methods (p. 249).

Even when diacetyl tartaric anhydride is distilled at atmospheric pressure (230-250°), a characteristic odor of carbon suboxide is noticeable and the distilled product is contaminated with acetic acid and

[45] Bagard, *Bull. soc. chim.* [4] 1, 307 (1907).
[46] LeSueur, *J. Chem. Soc.* 91, 1367 (1907).
[47] Prileshaiev, *J. Russ. Phys. Chem. Soc.* 39, 759 (1907); *Chem. Abstracts* 1, 2879 (1907).
[48] Ott and Schmidt, *Ber.* 55, 2126 (1922); Ott, *Ber.* 47, 2391 (1914).

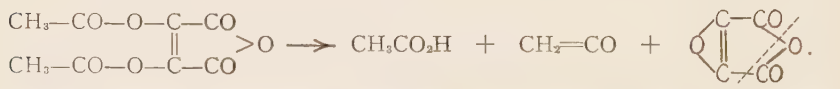
acetoxymaleic anhydride. This suggests the following steps in the pyrolysis:



As stated, the yield of carbon suboxide is over 40 percent, and the yield of acetic acid is 87 percent of the theoretical. If the yield of carbon suboxide is based on the diacetyltartaric anhydride that is actually decomposed, the value is 53.7 percent.

Acetoxymaleic anhydride decomposes much easier than diacetyl tartaric anhydride. With the former, there is vigorous decomposition at 140-150°, whereas the latter is quite stable at 150°. The former gives rise to 73 percent of the theoretical quantity of acetic acid and 37 percent of carbon suboxide when it is heated at a bath temperature of 130°. In another run, in which 0.39 gram of acetoxymaleic anhydride was heated by a free flame, 0.048 gram of carbon monoxide and 0.035 gram of carbon dioxide were identified. Thus for each mol of anhydride, 69.4 percent of a mol of carbon monoxide and 31 percent of a mol of carbon dioxide appeared.

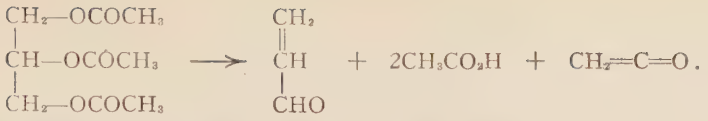
A different situation presents itself in diacetoxymaleic anhydride since no hydrogen appears to be available for the production of acetic acid. Yet, acetic acid is formed in its decomposition. Since ketene is formed also (10 percent yield), there is good evidence for the mechanism suggested by Ott:



Possibly acetic anhydride is formed momentarily. The hypothetical oxide of carbon is represented as breaking down into carbon suboxide and carbon dioxide. The yield of carbon suboxide is about 2 percent.

Triacetin is a somewhat similar case. When its vapors are decomposed by a hot platinum filament [49] using a bath temperature of 155°, and a vacuum as with diacetyltartaric anhydride, acrolein is formed in a 40 percent yield and ketene in a 26 percent yield.

[49] Ott, *Ber.* **47**, 2388 (1914).



In the presence of thoria, triacetin [50] decomposes at 460° and at 525° forming acrolein, a mixture of formic and acetic acids, diacetin, oxides of carbon, hydrocarbons, hydrogen and tars. In this case, ketene was not mentioned and presumably no attempt was made to establish its presence or absence. Tripropionin, treated similarly [51] at 420° and 510°, yields similar products, but it fails to yield any dipropionin. Nearly half of the tripropionin is undecomposed at the lower temperature. Acetic and propionic acids, but no formic, are the reported products. It would seem that tripropionin might be a reasonable source for methyl ketene, since triacetin is such a source for ketene. No study has been directed to this phase of the problem, however.

A convenient synthetic method for heptaldehyde and for undecylenic acid merely involves the vacuum distillation of *castor oil*. From one liter of oil there is formed 580 cc. of distillate and a foamy residue. It is essential that the distillation [52] be rapid (20-30 minutes). At the conclusion of the experiment the still-head temperature is 400°. Fractionation of the distillate yields 250 cc. of heptaldehyde and 120 cc. of undecylenic acid.

Esters of Aromatic Acids.

Methyl Benzoate.

No pyrolysis occurs with methyl benzoate [53] in 8 hours at 400°, whereas at 360° ethyl benzoate decomposes smoothly into ethylene and benzoic acid. Amyl benzoate changes into amylene at 340-350°. An application of this pyrolytic reaction is the partial dehydration of amyl alcohol by benzoic acid at 350°, which is explained by ester formation and then decomposition.

The comparative stability of methyl benzoate was also noted by Meyer and Hofmann.[54] It is only slightly decomposed by exposure to dull red heat, but at more elevated temperatures it produces benzene, diphenyl, methyl *m*- and *p*-phenylbenzoate, $C_6H_5—C_6H_4—CO_2CH_3$, and trioxymethylene. In methyl toluate, the *carbomethoxy* group is more stable than the *methyl* group since an important product of the de-

[50] Simons, *J. Am. Chem. Soc.* **48**, 1992 (1926).
[51] Simons, *ibid.*, p. 1993; for its earlier preparation, see Seuffert, *Z. Biol.* **61**, 551 (1913).
[52] Perkins and Cruz, *J. Am. Chem. Soc.* **49**, 1073 (1927).
[53] Engler and Low, *Ber.* **26**, 1440 (1893).
[54] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).

composition is methyl stilbene-4,4′-dicarboxylate, $(CH_3O_2C—C_6H_4—CH=)_2$. Trioxymethylene is also formed. It is difficult to reconcile Colson's statement [55] that methyl benzoate decomposes at 350° into carbon dioxide with these results. Colson also reported the slow decomposition of ethyl benzoate at 300° in a sealed tube into ethylene and benzoic acid; of ethyl salicylate (300°) into carbon dioxide and ethylene; and of methyl salicylate into carbon dioxide and anisole.

The benzoate of α,α,β-trimethylallyl alcohol, $\begin{matrix}(CH_3)_2C—C=CH_2\\ \quad|\quad\ |\\ \quad OH\ CH_3\end{matrix}$, is a thick oil that boils at 126° and 12 mm.; heating this ester at atmospheric pressure [55a] quickly converts it into benzoic acid and dimethyl butadiene, $\begin{matrix}CH_2=CH—C=CH_2\\ \qquad\quad|\quad\ |\\ \qquad\ CH_3\ \ CH_3\end{matrix}$.

Benzyl Benzoate.

To determine the effect of heat [56] on benzyl benzoate a sample of the ester, boiling point (21 mm.) 193-198°, weighing 42.5 grams was sealed in an evacuated tube and kept at 340-350° for 2 hours. After cooling overnight, the tube was found to have a high pressure. The liquid contents were black, and gave the following products: unchanged ester 21.5 grams, toluene 3 grams, benzaldehyde 2 grams, benzoic acid 2 grams, benzoic anhydride 3 grams, tars and residues 10 grams. There was no indication of stilbene, dibenzyl ether, diphenyl or phenanthrene.

The presence of toluene was indicated by the odor and the boiling point, 105-117°, and was confirmed by conversion to the dinitro derivative, melting point 68-70°. Since benzene, and not toluene, is the hydrocarbon which is formed from the similar pyrolysis of benzaldehyde (p. 241), this is evidence that the benzyl benzoate which was formed from the aldehyde escaped further decomposition under the conditions of the experiment.

The conclusion that benzoic anhydride was present rests on the following evidence. After removal of toluene, benzaldehyde and benzoic acid, there remained 24.5 grams of an alkali-insoluble residue. Twenty grams of this, on saponification, yielded 3 grams more of benzoic acid than should have come from 20 grams of benzyl benzoate. It gave 12 grams of benzoic acid and 7.5 grams of benzyl alcohol. The liquid absorbed a small amount of bromine without the evolution of

[55] Colson, *Compt. rend.* **148**, 643 (1909); **147**, 1054 (1908).
[55a] Claisen, Kremers, Roth and Tietze, *J. prakt. Chem.* **105**, 89 (1922).
[56] Hurd and Bennett, unpublished data.

hydrogen bromide. Benzoic anhydride [57] is known also to behave in this manner.

The formation of the benzaldehyde may be readily explained as a reversal of the Cannizzaro reaction:

$$C_6H_5CO_2CH_2C_6H_5 \longrightarrow 2C_6H_5CHO.$$

The benzoic acid may have come from this aldehyde by oxidation, or it may have been formed directly from the ester by thermal means. The simplest explanation to account for the presence of benzoic anhydride and toluene is to assume a disproportionation of two molecules of the ester into one of benzoic anhydride and one of dibenzyl ether:

$$\begin{matrix} C_6H_5—CO—O—CH_2C_6H_5 \\ + \\ C_6H_5—CO—O—CH_2C_6H_5 \end{matrix} \longrightarrow \begin{matrix} C_6H_5—CO \\ \\ C_6H_5—CO \end{matrix} >O + \left[O< \begin{matrix} CH_2C_6H_5 \\ \\ CH_2C_6H_5 \end{matrix} \right]$$

$$\left[O< \begin{matrix} CH_2—C_6H_5 \\ \\ CH_2—C_6H_5 \end{matrix} \right] \longrightarrow C_6H_5CHO + C_6H_5CH_3.$$

In other words, there appears to be a reaction tending to form molecules of greater symmetry. The dibenzyl ether pyrolyzes further into benzaldehyde and toluene, as has been expounded on p. 199.

Benzohydryl Benzoate.

Benzohydryl benzoate, $C_6H_5CO—O—CH(C_6H_5)_2$, is an ester that is very closely related to benzyl benzoate since neither the benzyl group nor the benzohydryl group exert a particularly strong electron attraction (p. 39). Both behave similarly when they are heated. If the ester, or rather, an intimate mixture of benzoic acid and benzohydrol, is distilled,[57a] benzoic acid, benzoic anhydride and tetraphenylethane are formed. Benzoic anhydride would be expected. Either tetraphenylethane or diphenyl-methane together with benzophenone would be the anticipated products if dibenzohydryl ether (p. 200) is to be regarded as a transitory product in this reaction. Likewise, it could be predicted that *triphenylmethyl benzoate,* $C_6H_5—CO—O—C(C_6H_5)_3$, would undergo pyrolysis into benzoic anhydride and bi-triphenylmethyl ether, or its products of pyrolysis.

The benzoate of chloretone,[58] $\begin{matrix} C_6H_5—CO—O—C(CH_3)_2 \\ | \\ CCl_3 \end{matrix}$, distils with partial decomposition at 250-270°. As would be expected, benzoic acid is one of the decomposition products but the fate of the trichloro-

[57] Gal, *Compt. rend.* **54**, 1228 (1862).
[57a] Linneman, *Ann.* **133**, 24 (1865); Anschütz, *Ann.* **235**, 220 (1886).
[58] Aldrich, *J. Am. Chem. Soc.* **42**, 1506 (1920).

*iso*butylene, which would also be expected, has not been studied. *l*-Menthyl benzoate yields [59] benzoic acid and *r*-menthene at 250°.

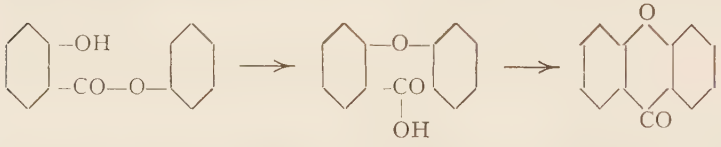
The monobenzoate, the *p*-nitrobenzoate, and the salicylate of glycol [60] all become quantitatively disproportionated into ethylene glycol and the di-ester at 300°:

$$2Ar{-}CO{-}O{-}CH_2{-}CH_2OH \longrightarrow (Ar{-}CO{-}O{-}CH_2{-})_2 + (-CH_2OH)_2.$$

One interesting feature of this pyrolysis is the almost complete lack of tendency for the formation of the acid, $Ar{-}CO_2H$, and acetaldehyde (through vinyl alcohol).

Salicylates, and the Production of Xanthones.

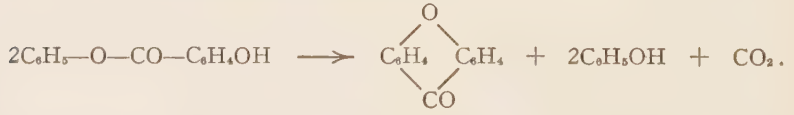
Earlier in this monograph (p. 444), salicylic acid has been shown to decompose into phenol, carbonic acid, phenyl salicylate and xanthone when heated. Phenyl salicylate is an intermediate in the change from salicylic acid to xanthone. Various mechanisms have been suggested to explain this change. Perhaps the simplest is Graebe's, which assumes an initial rearrangement into the phenyl ether of salicylic acid and a dehydration of the latter:



Phenol always accompanies this change, and its presence is explained [61] by hydrolysis of some of the unchanged phenyl salicylate:

$$C_6H_4(OH){-}CO{-}O{-}C_6H_5 + H_2O \longrightarrow 2C_6H_5OH + CO_2.$$

From 100 grams of salol, Graebe obtained 35-40 grams of phenol by heating the former to gentle boiling as long as any phenol distilled (6-7 hours), and 42-45 grams of crude xanthone. Recent directions [62] indicate a yield of 28-29 grams of purified xanthone, which is a 61-63 percent yield on the basis of the equation:



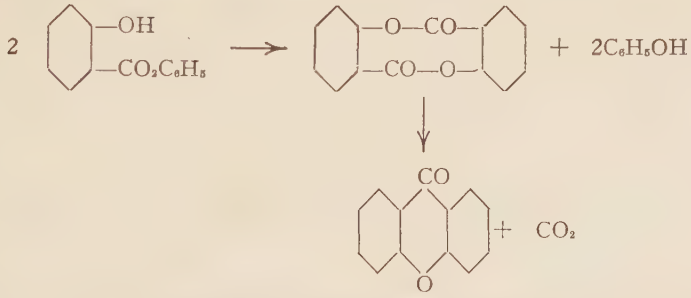
Although the phenyl ether of salicylic acid,[62] $C_6H_5{-}O{-}C_6H_4{-}CO_2H$, produces a small amount of xanthone at its distillation temperature (355°), it is a very unsatisfactory yield for purposes of argument

[59] Tschugajew, *Ber.* **35**, 2474 (1906).
[60] Cretcher and Pittinger, *J. Am. Chem. Soc.* **47**, 2560 (1925).
[61] Graebe, *Ann.* **254**, 282 (1889); Graebe and Feer, *Ber.* **19**, 2612 (1886).
[62] Holleman, "Organic Syntheses," Vol. VII, New York, John Wiley and Sons, 1927, p. 84.
[63] Graebe, *Ber.* **21**, 503 (1888).

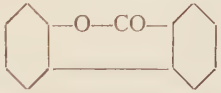
in support of Graebe's mechanism. The yield may be made quantitative, however, if sulfuric acid is employed as a dehydrating agent. The sodium salt of the ether-acid is made in 25-30 percent yields by heating the sodium derivative of salol for one hour at 280-300°;

In this connection, it may be pertinent to recall that the methyl ether of salicylic acid (p. 346) changes into a mixture of methyl salicylate and methyl-*o*-methoxybenzoate on distillation.

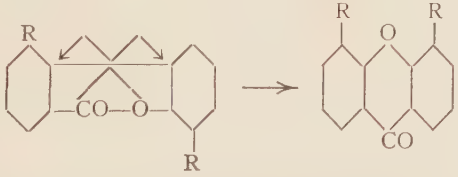
The alternative mechanism [64] to explain the formation of xanthone from phenyl salicylate stipulates that disalicylide is an intermediate product. Disalicylide is known to undergo pyrolysis into xanthone and carbon dioxide.



This reaction was studied [65] critically by Strohbach, who concluded that although part of the decomposition follows Graebe's mechanism, the major portion of it follows Seifert's. Recent work by Kunz-Krause and Manicke also supports this conclusion (p. 444).

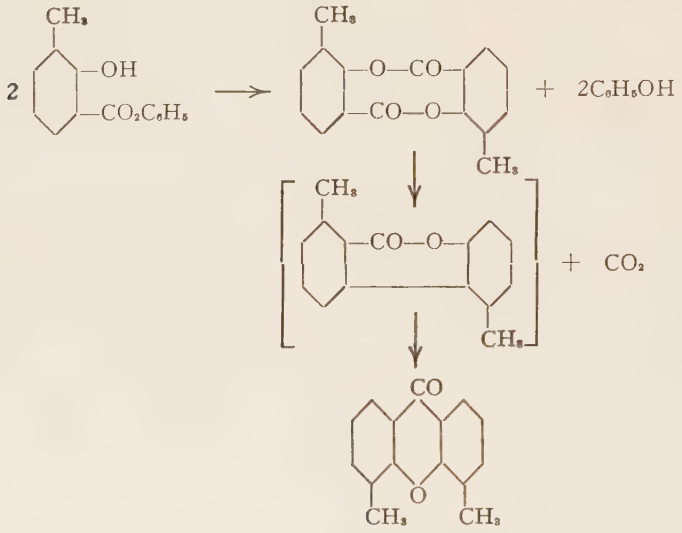
According to Strohbach, a δ-lactone, 

, is the necessary transition compound between disalicylide and xanthone. His conception of the mechanism of this change involves an inversion of one aromatic nucleus:



[64] Seifert, *J. prakt. Chem.* [2] **31**, 472 (1885); Kunz-Krause and Manicke, *Ber.* **53**, 190 (1920).
[65] Strohbach, *Ber.* **34**, 4136 (1901).

Evidence for this is the production [66] of 4,6-dimethylxanthone when phenyl *o*-cresotinate is heated:



4,6-dimethylxanthone

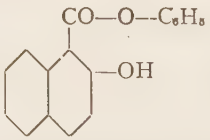
A lesser amount of 4-methylxanthone is also formed, but inasmuch as this is the only compound which would be anticipated from Graebe and Feer's conception:

$$CH_3—C_6H_3\langle \begin{matrix} OH \\ CO_2C_6H_5 \end{matrix} \longrightarrow CH_3—C_6H_3\langle \begin{matrix} OC_6H_5 \\ CO_2H \end{matrix} \xrightarrow{-H_2O} CH_3—C_6H_3\langle \begin{matrix} CO \\ O \end{matrix} \rangle C_6H_4$$

and,

$$CH_3—C_6H_3(OH)—CO_2C_6H_5 + H_2O \longrightarrow \begin{matrix} C_6H_5OH \\ + \\ CH_3—C_6H_4OH \end{matrix} + CO_2,$$

this indicates the insufficiency of Graebe's and Feer's mechanism. Schöpff obtained a 65 percent yield of 4,6-dimethylxanthone from *o*-cresyl *o*-cresotinate by boiling it as long as cresol was evolved and then distilling the xanthone.

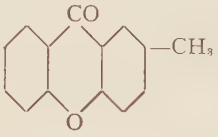
Phenonaphthoxanthone, $C_{10}H_6\langle \begin{matrix} CO \\ O \end{matrix} \rangle C_6H_4$, would be anticipated from phenyl β-hydroxynaphthoate, 

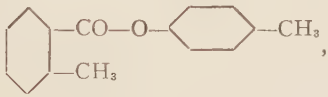
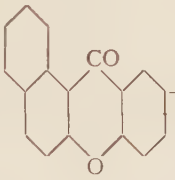
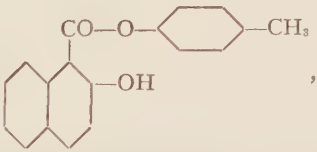
, by Graebe and Feer's reasoning, but Strohbach obtained good yields of dinaphtho-xanthone,

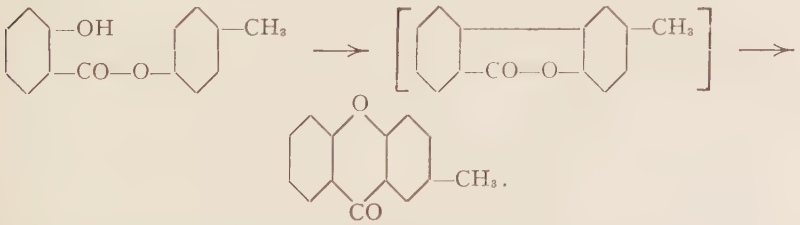
[66] Schöpff, *Ber.* **25**, 3644 (1892).

$C_{10}H_6<\begin{matrix}CO\\O\end{matrix}>C_{10}H_6$, instead. Large amounts of phenol are expelled in the early stages of the heating, and then at higher temperatures carbon dioxide is eliminated as the xanthone is formed.

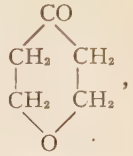
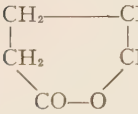
For such cases as the production of 2-methyl-xanthone,

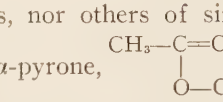


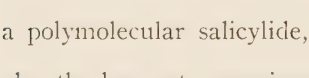
from *p*-cresyl salicylate,[61]  , or of 2-methyl-phenonaphtho-xanthone,[65]  , from *p*-cresyl-β-hydroxy-naphthoate,  , Graebe and Feer's mechanism is satisfactory. A strict adherence to Strohbach's mechanism would predict the formation of xanthone and of dinaphtho-xanthone instead of the unsymmetrical xanthones which are mentioned. This assumes, of course, the elimination of *p*-cresol in both cases, but the literature is silent regarding this feature. Strohbach's explanation of these cases assumes the direct formation of a δ-lactone, followed by inversion:

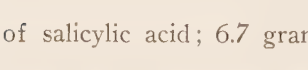
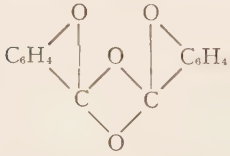
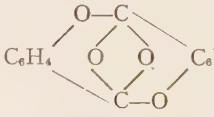


Whether or not this is a reasonable behavior for δ-lactones cannot be stated since almost nothing is known concerning their pyrolysis. The

mechanism would infer, however, that tetrahydro-γ-pyrone,  , would be formed during the thermal decomposition of valerolactone,  ; or better yet, that γ-pyrone would come from the lactone related to glutaconic aldehyde-acid:

Neither of these cases, nor others of similar nature, have ever been studied. 4,6-Dimethyl-α-pyrone,  , boils at 245°, but no mention [67] is made of its decomposition.

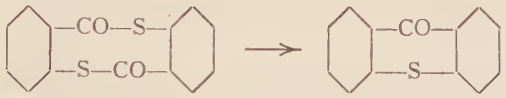
Aspirin, which is an acetate ester instead of a salicylate ester, melts with decomposition, the products [68] being acetic acid, salicylic acid, and a polymolecular salicylide,  . Like the acetyl derivative, so also the benzoate, propionate, and butyrate also undergo decomposition at their melting points giving, in turn, benzoic, propionic or butyric acids, and the polymeric salicylide, the molecular complexity of which is considered to be six to ten times that of the salicylide.

Previously, Anschütz [69] had determined that aspirin changes into the disalicylide by distillation at 20 mm. From 36 grams of aspirin, 1 gram of residual matter remains and the products of distillation are: 8.3 grams of acetic acid, and a little acetic anhydride; 5.3 grams of salicylic acid; 6.7 grams of α-disalicylide,  ; 5.9 grams of β-disalicylide, for which Anschütz suggested the formulas:  , or  ; and 5.0 grams of polymers. β-Disalicylide is somewhat transformed into α-disalicylide by

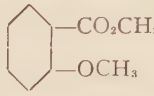
[67] Hantzsch, *Ann.* **222**, 16 (1883).
[68] Paolini, *Giorn. chim. ind. applicata* **3**, 403 (1921); *Chem. Abstracts* **16**, 314 (1922); Paolini and Scelba, *Atti accad. Lincei* (v) **31**, i, 378 (1922).
[69] Anschütz, *Ber.* **52**, 1883 (1919).

distillation at 12-20 mm., whereas at atmospheric pressure both give carbon dioxide and xanthone. The yield of xanthone by heating aspirin [70] at atmospheric pressure to 350° is 40 percent. This is a modification of Perkin's procedure,[71] in which salicylic acid is mixed with acetic anhydride and heated.

Dithio-disalicylide is partially converted [72] into thioxanthone at its melting point, 170°:



Anschütz (*loc. cit.*) studied not only the effect of heat on acetyl salicylic acid, but also on salicoyl salicylic acid, or "diplosal".

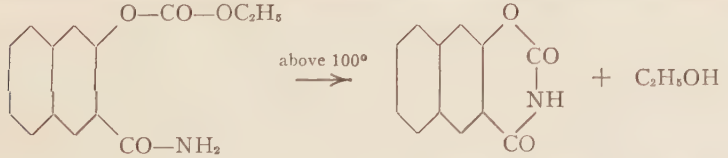
Methyl salicylate [73] gives a 60-70 percent yield of anisole, 5 percent of phenol and some resin when it is maintained for 2-3 hours in a sealed tube at 340-350°. The methyl ether of methyl salicylate, on the other hand, 

, is unchanged after 4 hours at 400-430°. Ethyl salicylate pyrolyzes like the methyl ester and gives phenetole. The gaseous products are 64 percent carbon dioxide and 1 percent carbon monoxide. By heating methyl *p*-methoxybenzoate for 2 hours at 430°, the decomposition proceeds to the formation of carbon dioxide, ethylene, anisole, some carbon and resin (see p. 346). In addition to the formation of xanthone and phenol from salol, Ipatiew identified a little diphenyl ether (temperature 420°).

Esters of Dibasic Acids.

Carbonates.

Little is known of the pyrolysis of the simple alkyl or aryl carbonates. In the following cases, the course of the decomposition may undoubtedly be traced through another functional group in the molecule.



1,4-diketo-3,4-dihydro-lin-*naphtho-1,3-oxazine* [74]

[70] Simon, *Bull. soc. chim. biol.* **8**, 203 (1926); *Chem. Abstracts* **20**, 2680 (1926).
[71] Perkin, *Ber.* **16**, 338 (1883).
[72] Anschütz and Rhodius, *Ber.* **47**, 2733 (1914).
[73] Ipatiew, Orlov, Petrov, *Bull. soc. chim.* **39**, 664 (1926).
[74] Fries, *Ber.* **58**, 2845 (1925).

Compounds such as the "ethyl carbonate of butyl-*o*-hydroxycarbanilate",

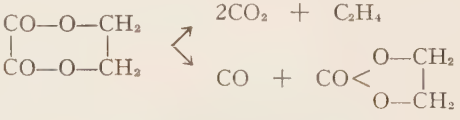
, have been found [75] to change into non-isomeric crystalline substances by vacuum distillation, concerning which little is known as yet.

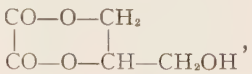
Oxalates.

Ethyl hydrogen oxalate may be distilled in a vacuum, but at atmospheric pressure it changes [76] on distillation chiefly into ethyl formate and carbon dioxide. The fact that ethyl hydrogen oxalate decomposes at about 140° makes the preparation of diethyl oxalate difficult unless the water formed in the esterification is removed below this temperature. Hultman, Davis and Clarke [77] have ingenuously avoided this difficulty by adding carbon tetrachloride to "steam-distil" away the water as fast as it is formed.

In a sealed tube at 250°, 10 cc. of ethyl oxalate [78] forms one liter of gas, 48.4 percent of which is carbon monoxide, 43.8 percent carbon dioxide, and 7.8 percent olefines. The addition compound of sodium ethylate to ethyl oxalate, presumably possessing [79] the structure, $(C_2H_5O)_2C(ONa)—CO_2C_2H_5$, decomposes at 115°, or in hot xylene, into ethyl carbonate, carbon monoxide, and an alkaline residue.

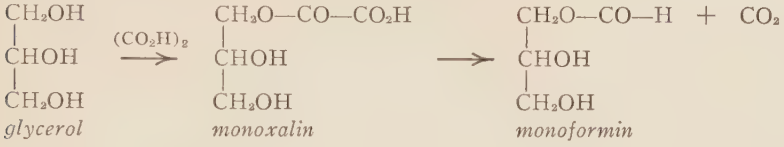
At 241°, ethylene oxalate is 40 percent pyrolyzed [80] into carbon dioxide and ethylene, and 28 percent into carbon monoxide and ethylene carbonate:



Glyceryl oxalate (dioxalin),  , melts with decomposition at 220-225°, yielding allyl alcohol, oxides of carbon, and a thick oil which may be glyceryl carbonate. Chattaway [76] believes that dioxalin is the exclusive precursor of allyl alcohol in the interaction of glycerol and oxalic acid. His interpretation of the formation of formic acid, allyl alcohol, and small yields of allyl formate are as follows. Carbon

[75] Nelson and Aitkenhead, *J. Am. Chem. Soc.* **48**, 1682 (1926).
[76] Chattaway, *J. Chem. Soc.* **105**, 152 (1914).
[77] Hultman, Davis and Clarke, *J. Am. Chem. Soc.* **43**, 369 (1921).
[78] Engler and Grimm, *Ber.* **30**, 2922 (1897).
[79] Adickes, *Ber.* **58**, 1992 (1925).
[80] Tilicheiev, *Ber.* **56**, 2218 (1923).

dioxide appears at the early stages of the heating, and carbon monoxide is liberated freely at higher temperatures.



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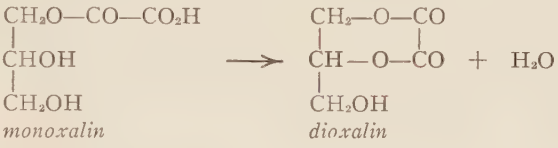
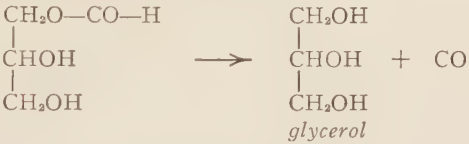


The monoformin behaves as follows:



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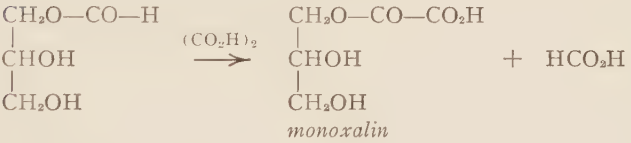
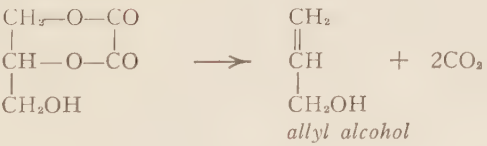


The dioxalin also either pyrolyzes directly or reacts with oxalic acid:



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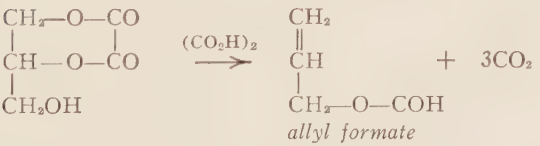


Chattaway's evidence for these steps is based on an analysis of the reaction mixture (glycerol and oxalic acid, heated at 80-90° for a few hours, then to 180° in a vacuum) for dioxalin and then obtaining from it a yield of allyl alcohol closely approximating the theoretical, based on the dioxalin present. Thus, 252 grams of the reaction mixture contained 26.8 grams of dioxalin, and this should have yielded 10.6 grams of allyl alcohol. Actually, 9 grams of allyl alcohol was isolated from the

24.5 grams of distillate which resulted as the mixture was heated to 270° at atmospheric pressure.

The most potent objection that can be raised against Chattaway's assertion that "the chief, if not the sole, source of the allyl alcohol is the normal oxalic ester, dioxalin", is that allyl alcohol is prepared in better yields (p. 526) from glycerol and formic acid than from glycerol and oxalic acid. Practically, if formic acid is desired from oxalic acid by this method, the temperature does not exceed 110°, and the glycerol functions as a catalyst since it is constantly regenerated. If allyl alcohol is desired, the temperature reaches 260°; the glycerol is not regenerated; and the relative weights of glycerol and oxalic acids usually employed are in the ratio of 4 to 1.

Tilicheev[81] has furnished evidence for the structure of glyceryl oxalate as $\begin{matrix} CO{-}O{-}CH_2 \\ | \qquad\quad | \\ CO{-}O{-}CH{-}CH_2OH \end{matrix}$, since there was no indication of cyclopropanol in its pyrolysis as would be anticipated from the alternative formula. The yield of allyl alcohol was found to be about 60 percent. The same investigator also studied the action of heat on trimethylene oxalate and on other cyclic esters of dibasic acids which will be mentioned in their proper place. Trimethylene oxalate appears to decompose through a transient molecule of trimethylene glycolyl carbonate. From 39.6 grams of the trimethylene oxalate, 3950 cc. of carbon monoxide were obtained and 2.2 grams of trimethylene glycol. Other products obtained were 10.8 grams of carbon dioxide and some propionaldehyde. The reaction proceeds as follows:

Trimethylene Oxalate — *Trimethylene Glycolyl Carbonate*

$$CO + CO_2 + C_2H_5CHO$$

Propionaldehyde

Ethylene oxalate, in addition to the decomposition that has already been mentioned, may be converted into a dimer (of higher melting point) by vacuum distillation.

Bi-trichloromethyl oxalate,[82] $Cl_3C{-}O{-}CO{-}CO{-}O{-}CCl_3$, breaks down by heating into carbon monoxide and phosgene ($CO + 3COCl_2$).

A convenient method of synthesis for the mixed "oxalic ester-oxalyl

[81] Tilicheev, *J. Russ. Phys. Chem. Soc.* **58**, 447 (1927); *Chem. Abstracts* **21**, 3358 (1927).
[82] Cahours, *Ann. phys. chim.* [3] **19**, 352 (1847).

chloride" is the thermal decomposition of the dichloride formed by the interaction of ethyl oxalate and phosphorus pentachloride which occurs with moderate heating. Anschütz recommended [83] the use of small quantities (5.7 grams) during the heating for 1 hour at 165-170° (giving 3.2 grams of ethoxalyl chloride):

$$C_2H_5O—CO—CCl_2—OC_2H_5 \longrightarrow C_2H_5O—CO—CO—Cl + C_2H_5Cl.$$

The author has found that this is unnecessary, and unless a product of very high purity is desired, it is not necessary even to purify the dichloro ester prior to its decomposition. Instead,[84] the phosphoric chlorides are distilled away at 124-128° and at 134-136°, ethyl chloride is evolved and the desired ester-chloride distils. Barré has supplied [85] a modification of Anschütz' method for the preparation of ethoxalyl chloride. The best yield (84 percent) was obtained by operating at 110-115° for 13 hours. Stirring was employed, and the products carried off by the escaping ethyl chloride were recovered.

Malonates and Bromo Esters.

Ethyl hydrogen malonate [86] resembles malonic acid in becoming decarboxylated at 150°. However, ethyl acetate is not the sole product, for diethyl malonate and acetic acid also appear, an indication of disproportionation:

$$2C_2H_5O_2C—CH_2—CO_2H \longrightarrow CH_2(CO_2C_2H_5)_2 + [CH_2(CO_2H)_2]$$
$$[CH_2(CO_2H)_2] \longrightarrow CH_3CO_2H + CO_2$$

The acid esters of malonic acid are much less stable than the normal esters.

In contrast to the instability of $=C(CO_2H)_2$, or of $=C<^{CO_2H}_{CO_2R}$, a remarkable stability towards heat appears with the grouping, $=C(CO_2R)_2$. Ethyl malonate withstands fairly high temperatures before becoming altered. Its vapors are changed by a white hot platinum wire [87] into ethylene, and the decomposition products of malonic acid, namely, methane and carbon dioxide. The tetraethyl ester of ethylene-tetracarboxylic acid,[88] $(C_2H_5O_2C)_2C=C(CO_2C_2H_5)_2$, boils at 325° with only a partial decomposition. Carbon dioxide is said to be evolved to a certain extent.

[83] Anschütz, *Ann.* **254**, 26 (1889).
[84] Hurd, unpublished data.
[85] Barré, *Bull. soc. chim.* **41**, 47 (1927).
[86] Marguery, *Bull. soc. chim.* [3] **33**, 544 (1905).
[87] Wilsmore and Stewart, *Proc. Chem. Soc.* **23**, 309 (1908).
[88] Conrad and Guthzeit, *Ann.* **214**, 77 (1882).

Dimethyl α-bromo β-phenyl-γ-benzoyl-ethylmalonate,[89] $C_6H_5COCH_2$—$CH(C_6H_5)$—$CBr(CO_2CH_3)_2$, is less than half decomposed after two hours' heating at 200° under diminished pressure. Whatever pyrolysis there is, takes place not at the ester grouping but at other positions in the molecule. This is apparent from the list of compounds which are formed, all of which may be readily interpreted: bromine; hydrogen bromide; the unbrominated ester, $C_6H_5COCH_2CH(C_6H_5)$—$CH(CO_2CH_3)_2$; ethyl malonate; and some benzalacetophenone dibromide.

An interesting α-bromomalonate[90] is the methyl ester of α-bromo-β-hydroxy-*iso*propyl malonic acid lactone, which changes into methyl bromoketene when it is slowly distilled at 5 mm. pressure at 95°. The ketene rapidly polymerizes.

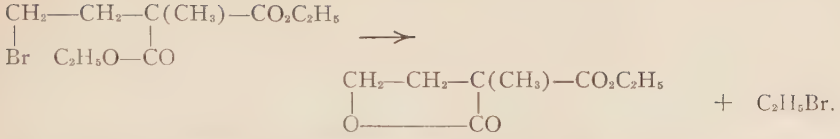
$$(CH_3)_2C(O{-}CO){-}CBr{-}CO_2CH_3 \longrightarrow (CH_3)_2CO + CBr{-}CH_3{=}CO + CO_2$$

Related reactions have already been discussed on p. 365.

Although the malonic ester grouping is *stable* so far as itself is concerned, it is *reactive* towards special groups which may be present in the molecule. Towards γ-halogen atoms, for example, it undergoes ring-closure. This property is shared by all γ-halogenated esters. Another of Kohler's compounds,[91] methyl γ-bromo-β-phenyl-γ-benzoyl-ethylmalonate, illustrates this point very well. The only difference between this compound and the earlier one is the position of the bromine atom, yet the γ-bromo compound is completely decomposed in 2 hours at 190°. Bromine, hydrogen bromide and methyl bromide are evolved, and from 20 grams of the original ester, Kohler isolated 8 grams of the ketolactonic ester, $C_6H_5CO{-}CH(O{-}CO){-}CH(C_6H_5){-}CH(CO_2CH_3)$, and a smaller quantity of the unbrominated ester, $C_6H_5COCH_2$—$CH(C_6H_5)$—$CH(CO_2CH_3)_2$. By working in a vacuum of 8 mm., first at 150° and then at 125°, an 80 percent yield of the lactone was realized.

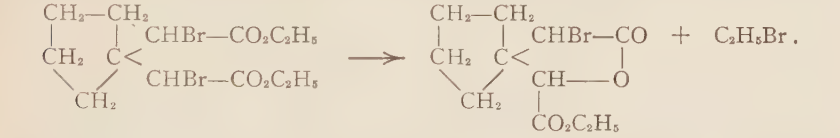
At 200-210°, γ-bromoethyl *iso*succinic ester[92] loses ethyl bromide and forms α-methylbutyrolactone-carboxylic ester. The yields obtained in this pyrolysis indicate that it follows the equation almost quantitatively:

[89] Kohler, *J. Am. Chem. Soc.* **44**, 846 (1922).
[90] Ott, *Ann.* **401**, 159 (1914).
[91] Kohler, *J. Am. Chem. Soc.* **44**, 840 (1922).
[92] Marburg, *Ann.* **294**, 104 (1897).



The γ-chloro compound behaves analogously and shows no tendency for HCl elimination with the formation of an unsaturated compound. This is in contrast to Bredt's reported formation of an unsaturated ester [93] and hydrogen chloride when γ-chloro-*iso*caproic ester is heated.

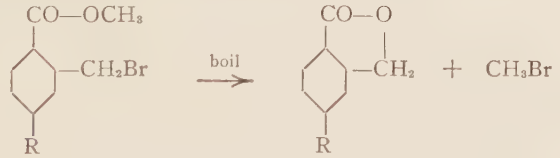
The following compound is related to ethyl glutarate rather than to ethyl malonate, but it resembles the cases in question in having a γ-bromine atom. It is noteworthy that the ester also contains an α-bromine atom and that this α-atom is inert during the process:



The lactone (both *cis* and *trans* forms of it) results [94] from repeated distillation at 211° and 30 mm. About 10 percent yield is formed at each distillation. Under similar circumstances, the corresponding cyclohexane compound lactonizes completely as ethyl bromide is evolved.

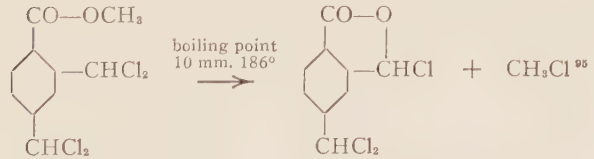
The following cases are self-explanatory.

(1)



(R=CH_3— or —CH_2Br) *4-methyl-1,2-phthalide*

(2)



(3)

(a) Where R = Br, heat at 120° and 30-40 mm. for 2-3 hours. Under these conditions the corresponding chlorine [96] compound (R = Cl) is stable.

[93] Bredt, *Ber.* **19**, 515 (1886).
[94] Becker and Thorpe, *J. Chem. Soc.* **117**, 1579 (1920).
[95] Perkin and Stone, *J. Chem. Soc.* **127**, 2275 (1925).
[96] Wolff and Schwabe, *Ann.* **291**, 231, 234 (1896).

(b) Where R = CH_3, heat for 2 hours at 120° in an open flask.[97]

(4) $BrCH_2{-}CO$ $\quad\quad$ $CO{-}CH_2Br$[98]
$\quad\quad\quad\quad >CH{-}CH<$ $\longrightarrow$ $2C_2H_5Br$ +
$C_2H_5O{-}CO$ $\quad\quad$ $CO{-}OC_2H_5$

$CH_2{-}CO$ $\quad\quad$ $CO{-}CH_2$
$\quad\quad >CH{-}CH<$
$O{-}{-}CO$ $\quad\quad$ $CO{-}O$.

Ethyl dibromotricarballylate possesses halogens in the α, β and γ positions to the carbethoxy groups, and from the foregoing one would surmise a preferential reaction with a γ-halogen. Instead of a γ-lactone, however, Ingold, Oliver and Thorpe[99] reported a β-lactone for the decomposition product, and two alternative formulas for it were suggested:

$Br{-}CH{-}CO{-}OC_2H_5$
$\quad\quad|$
$Br{-}C{-}CO{-}OC_2H_5$ $\xrightarrow[\text{distillation}]{\text{vacuum}}$ C_2H_5Br +
$\quad\quad|$
$\quad CH_2{-}CO{-}OC_2H_5$

Ethyl dibromotricarballylate

$BrCH{-}CO$ $\quad\quad$ $CH{-}CO{-}OC_2H_5$
$\quad|\quad/$ $\quad\quad\quad|\quad/$
$\quad|\ O$ $\quad\quad\quad|\ O$
$\quad C<$ $\quad\quad\quad|$
$\quad|\quad CO{-}OC_2H_5$ *or* $\quad Br{-}C{-}CO$
$\quad|$ $\quad\quad\quad\quad|$
$CH_2{-}CO{-}OC_2H_5$ $\quad\quad$ $CH_2{-}CO{-}OC_2H_5$.

Lactone ester of bromohydroxy-tricarballylic acid

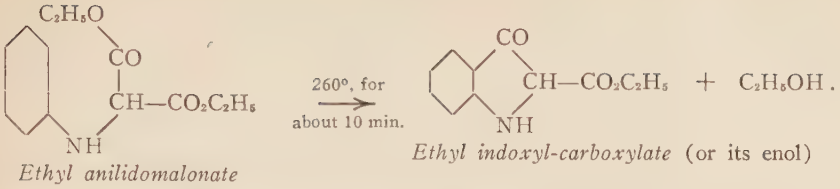
The alternative γ-lactone, $O{-}{-}CH{-}CO_2C_2H_5$ / $CBr{-}CO_2C_2H_5$ / $CO{-}CH_2$, seems not to have been considered. In this reaction it was definitely established that bromine was not eliminated with the production of aconitic ester.

Another halogeno-ester, although of a different type, is triacetyl-aurin chloride. This substance[100] begins to give off acetyl chloride at 120°, more rapidly at 160°, until one molecule of acetyl chloride has been lost. The residual product is undoubtedly diacetyl aurin.

$(CH_3CO{-}O{-}C_6H_4)_3C{-}Cl$ $\longrightarrow$ CH_3COCl +
$(CH_3CO{-}O{-}C_6H_4)_2C{=}C_6H_4{=}O$.

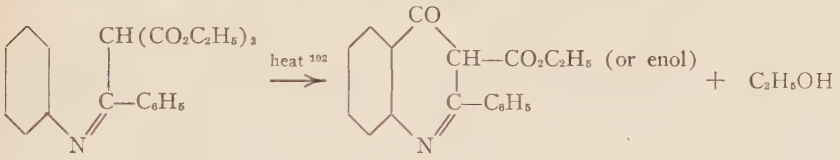
A few cases bear witness to ring closures in which ester groupings react with a hydrogen of an aromatic nucleus. Thus:

[97] Wolff and Erbstein, *Ann.* **288**, 16 (1895).
[98] Wolff, *Ann.* **399**, 309 (1913).
[99] Ingold, Oliver and Thorpe, *J. Chem. Soc.* **125**, 2128 (1924).
[100] Gomberg and Snow, *J. Am. Chem. Soc.* **47**, 205 (1925).

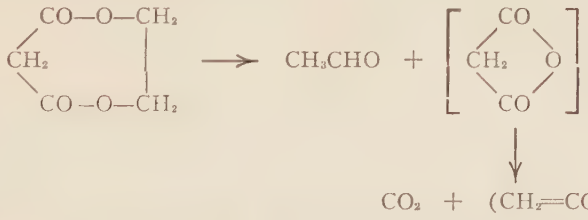


Ethyl anilidomalonate — *Ethyl indoxyl-carboxylate* (or its enol)

The *p*-toluido- and the *β*-naphthalido-analogs [101] behave similarly.



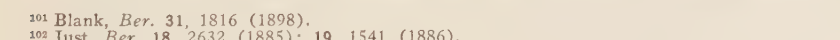
Vacuum distillation [103] of *ethylene malonate* (3 mm.) leads to the formation of a dimer. The cyclic ester starts to undergo pyrolysis at 205°, and from 300 grams there was formed 133.5 grams of distillate, 66.8 grams of a carbon residue, and gases. Carbon dioxide was almost the exclusive gaseous product. In the distillate were found 4.3 grams of ethyl acetate and 28.3 grams of glycol diacetate. There was evidence for the following mechanism:



Ketene was not found as such, though its polymers may have been in the tarry residue.

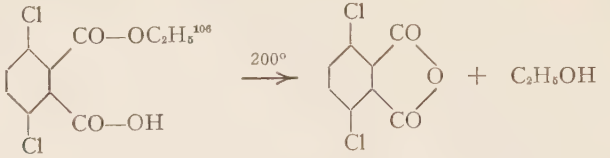
Succinates, and Related Dibasic Esters.

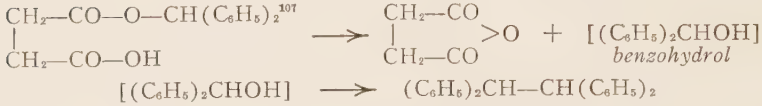
Monoethyl succinate [104] boils at 172° in a vacuum of 42 mm. with partial decomposition into diethyl succinate and succinic acid (or anhydride). A similar but more pronounced disproportionation is noticed [105] with monoethyl sebacate when distilled at atmospheric pressure:



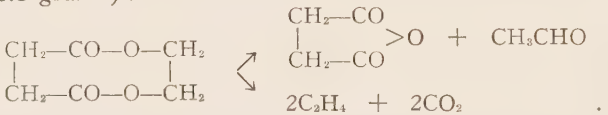
[101] Blank, *Ber.* **31**, 1816 (1898).
[102] Just, *Ber.* **18**, 2632 (1885); **19**, 1541 (1886).
[103] Tilicheev, *J. Russ. Phys. Chem. Soc.* **58**, 447 (1927); *Chem. Abstracts* **21**, 3358 (1927).
[104] Blaise, *Bull. soc. chim.* [3] **21**, 643 (1899).
[105] Grün and Wirth, *Ber.* **55**, 2206 (1922).

Ring closure, however, occurs in the following cases.



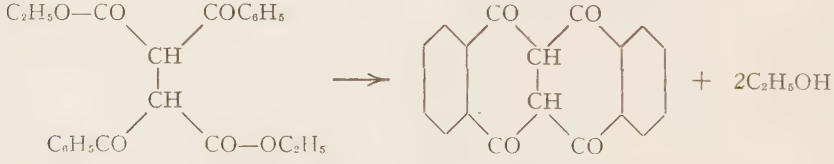


Two reactions occur[108] in the distillation of ethylene succinate (29.3 grams), one yielding acetaldehyde (0.58 gram) and succinic anhydride (2 grams) and the other, ethylene (0.2 gram) and carbon dioxide (6.8 grams):



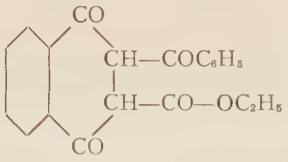
This pyrolysis starts by ordinary distillation at 310° and becomes vigorous at 350-355°. The decomposition is not clean-cut since water, a carbonaceous residue and an oil, boiling point 160-205°, are also produced. Quite different products result from distillation at bath temperatures of 340-360-390° in a vacuum of 3-6 mm. Succinic anhydride is again produced (2.5 grams from 15.4 grams of ester) but the major portion (10 grams) of the distillate is an isomer of the ester whose melting point is about 40° higher than that of the original ester. Its structure is undetermined. If the pyrolysis of ethylene succinate is compared with that of ethylene malonate it will be seen that the latter gives much more carbon dioxide.

Three hundred grams (60 grams recovered) of dibenzoyl-succinic ester,[109] best distilled in 5 gram portions, yields 40 grams (pure) of a quinone type of compound. This decomposition starts at 180° and is completed at 280°.



[106] Graebe, *Ber.* **33**, 2021 (1901).
[107] Anschütz, *Ann.* **235**, 220 (1886); *see also* Linnemann, *Ann.* **133**, 24 (1865). Compare p. 160, this monograph, for the production of tetraphenylethane from benzohydrol.
[108] Tilicheev, *J. Russ. Phys. Chem. Soc.* **57**, 143 (1925); *Chem. Abstracts* **20**, 2823 (1926); *J. Russ. Phys. Chem. Soc.* **58**, 447 (1927); *Chem. Abstracts* **21**, 3358 (1927).
[109] Knorr and Scheidt, *Ber.* **27**, 1167 (1894); Knorr, *Ann.* **293**, 110 (1896).

Four grams of material, shown to be the mono-quinone,



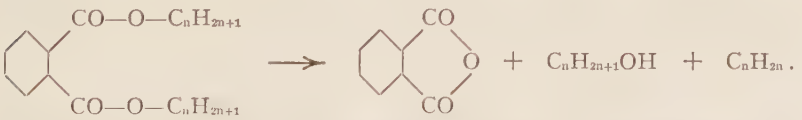
also appears as a by-product. One might suspect that dibenzoyl-*iso*succinic ester, $(C_6H_5CO)_2CH—CH(CO_2C_2H_5)_2$, would also form these identical products.

Dibenzoyl-maleic ester isomerizes [110] into dibenzoyl-fumaric ester above its melting point, or better by heating in aniline at 100°. Either one or two mols [111] of carbon dioxide may be expelled from diphenyl fumarate by gradual distillation. In consequence, phenyl cinnamate or stilbene is formed:

$$C_6H_5O_2C—CH=CH—CO_2C_6H_5 \longrightarrow C_6H_5—CH=CH—CO_2C_6H_5 \longrightarrow C_6H_5—CH=CH—C_6H_5.$$

Cases like this, wherein carbon dioxide is eliminated from an ester, followed by simple union of the two residues, are comparatively rare. Such a reaction has been mentioned in connection with the preparation of methyl bromoketene (p. 550). Carbon dioxide is also liberated from ethylene oxalate, ethylene malonate and ethylene succinate and a few aromatic esters (p. 538). It will be shown that this is also true of some α-amino esters and some heterocyclic esters. Anschütz has found that stilbene derivatives, but not cinnamates, are formed by heating *p*-cresyl fumarate or *p*-bromophenyl fumarate at 240-245°. Diphenyl succinate was found to give only a little of symmetrical diphenyl ethane.

With the exception of dimethyl phthalate, all of the alkyl phthalates are unstable at the boiling point.[112] The general equation of pyrolysis is:



The mixed esters, which contain a methyl radical, yield methanol and the olefine derived from the other ester radical. The velocity of the reaction increases with the length of the carbon chain of the alkyl group, and is greater with tertiary groups than with secondary.

[110] Paal and Schulze, *Ber.* **33**, 3792 (1900).
[111] Anschütz, *Ber.* **18**, 1945, 1947 (1885); **60**, 1320 (1927).
[112] Nagel and Abelsdorff, *Wiss. Veröffentlich. Siemens-Konzern* **5**, 193 (1926); *Chem. Abstracts* **21**, 1642 (1927).

Keto Esters.

α-Keto Esters.

Most of the α-keto esters which have been studied for their behavior towards heat possess a γ-carbonyl group as well as an α-, but quite customarily, the mode of decomposition is a simple elimination of the α-carbonyl as carbon monoxide. The following equation expresses this behavior:

$$\Phi\text{—CO—CH}_2\text{—CO—CO}_2\text{R} \longrightarrow \Phi\text{—CO—CH}_2\text{—CO}_2\text{R} + \text{CO.}$$

(Φ = phenyl, ethoxy, etc.)

One important application of this reaction is in the well-known synthesis of ethyl phenylmalonate, a compound which cannot be directly synthesized from ethyl malonate. Instead, ethyl phenylacetate and ethyl oxalate are condensed in the presence of sodium ethylate, and the resulting keto-ester [113] is decomposed by distillation under diminished pressure:

$$\begin{array}{l} C_6H_5\text{—CH—CO}_2C_2H_5 \\ \quad\quad\quad\ \ | \\ \quad\quad\quad\ \ CO\text{—CO}_2C_2H_5 \end{array} \xrightarrow[20\text{-}40\ \text{mm.}]{170\text{-}190^\circ} C_6H_5\text{—CH(CO}_2C_2H_5)_2 + \text{CO.}$$

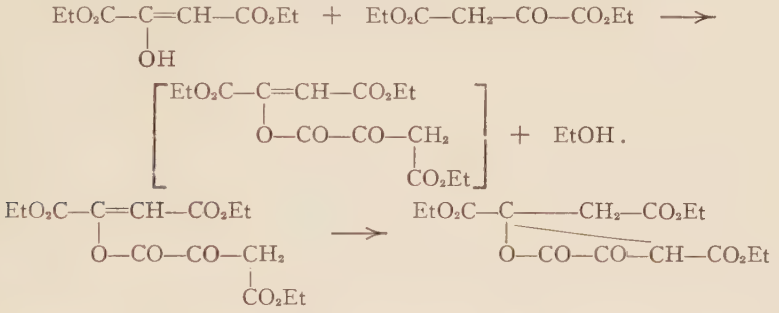
Ethyl ethoxyoxaloacetate,[114] $C_2H_5O - CH(CO_2C_2H_5) - CO - CO_2C_2H_5$, forms ethyl ethoxymalonate and nearly the theoretical amount of carbon monoxide by heating in a carbon dioxide atmosphere at 180-200°. In this connection, Watson [115] has recently shown that this decomposition, and also that of ethoxy-oxalopropionic ester and of ethoxyoxalosuccinic ester, follows the unimolecular law between 140-200°. The reaction is unaffected by such solvents as bromonaphthalene and nerolin, or by hydrogen chloride gas, or by moisture. An excess of carbon monoxide, however, retards it. The velocity constant is found to vary with the temperature according to the Arrhenius law, $k = Ae^{-Q/RT}$, and if A is the probability per second that an active molecule will decompose,[116] a relation is expected for similar compounds and Watson finds $Q/\log A$ is constant..

Distillation of ethyl oxaloacetate [117] at ordinary pressure yields ethyl malonate as the chief reaction product. This would be expected. The gas evolution starts at 160° and proceeds vigorously at 190°:

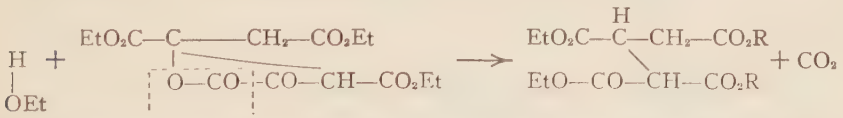
$$C_2H_5O_2C\text{—CO—CH}_2\text{—CO}_2C_2H_5 \longrightarrow \text{CO} + \text{CH}_2(\text{CO}_2C_2H_5)_2.$$

[113] Wislicenus, *Ber.* **27**, 1093 (1894).
[114] Wislicenus and Münzesheimer, *Ber.* **31**, 551 (1898).
[115] Watson, *Proc. Roy. Soc.* (London) **108A**, 132 (1925).
[116] Compare Christiansen, *Z. physik. Chem.* **103**, 91 (1922); Christiansen and Kramers, *ibid.* **104**, 451 (1923).
[117] Wislicenus, *Ber.* **27**, 795 (1894).

In addition, some carbon dioxide, ethanol, ethyl pyruvate, $CH_3COCO_2C_2H_5$, and some high boiling esters of undetermined structure are also formed. It would be difficult to interpret the course of the side reactions from these data alone, but from Gault's results [118] it is evident that other types of reaction do participate in the change. Gault found that a 70-80 percent yield of oxalocitric lactone was obtainable by maintaining ethyl oxaloacetate for 4 hours at 150°. It seems that this reaction must proceed through the enol form of the ester:

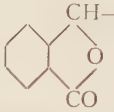


Furthermore, if this lactone ester is distilled [119] in a vacuum (210-216° and 30 mm.), there is formed a 45-50 percent yield of tricarballylic ester, and 70-80 percent of the theoretical amount of carbon dioxide. Gault assumes that alcohol is first liberated, and then it reacts with the lactone-ester in accordance with the following equation:



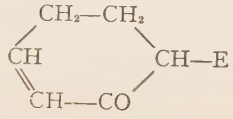
This decomposition takes place to a noticeable extent even at 130-150° during the distillation.

In Table LIV is a record of the behavior of similar compounds. In all cases, the chief reaction is a simple elimination of carbon monoxide. A recent patent [120] recommends coke or pumice as a contact mass for the conversion of oxalylacetic esters into malonic esters at temperatures between 250-350°.

The α-ketonic ester [121] related to phthalide,  , is quite stable. It scarcely decomposes even at 300°, and the resulting

[118] Gault, *Compt. rend.* **158**, 711 (1914).
[119] Gault, *Compt. rend.* **158**, 632 (1914); **159**, 256 (1914).
[120] Brit. Pat. 228,863, *Chem. Abstracts* **19**, 2960 (1925).
[121] Wislicenus and Münzesheimer, *Ber.* **31**, 556 (1898).

TABLE LIV. *Pyrolysis of α-Keto Esters.*

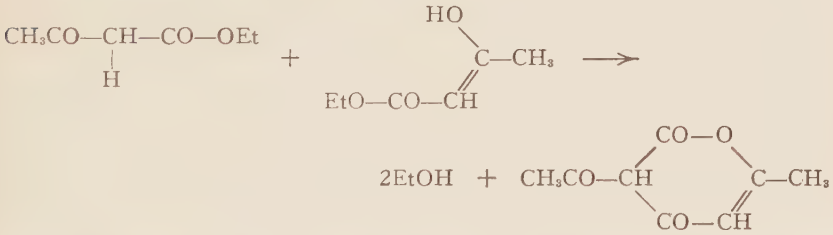
Formula	Conditions	Resulting Ester	Reference
$-E=-CO-CO-OC_2H_5$			
$C_6H_5-CO-CH_2-E$	230-250°	Ethyl benzoylacetate	Wislicenus, *Ber.* **28**, 813 (1895).
E—E	Heat	Ethyl ketomalonate, and ethyl oxalate	Anschütz and Pauly, *Ber.* **27**, 1304 (1894).
$CH_3-CH(CO_2C_2H_5)-E$	Distillation at atmospheric pressure	Diethyl methylmalonate	Wislicenus, *Ber.* **27**, 796 (1894).
$C_6H_5CH_2-CH(CO_2C_2H_5)-E$	200°	Ethyl benzylmalonate	Wislicenus and Münzesheimer, *Ber.* **31**, 555 (1898).
$C_2H_5O_2C-CH(CH_2-CO_2C_2H_5)-E$	140-170° (some, by vacuum distillation)	Ethyl carbethoxysuccinate	Wislicenus, *Ber.* **27**, 796 (1894).
$C_2H_5O_2C-CH(CH_2-CO_2C_2H_5)-CH(CO_2C_2H_5)-E$	Vacuum distillation	Ethyl ethane-tetracarboxylate	Wislicenus and Boeckler, *Ann.* **285**, 20 (1895).
$C_2H_5O_2C-CH(CH_2-CO_2C_2H_5)-CH(CO_2C_2H_5)-E$	Vacuum distillation	Ethyl α-carbethoxyglutarate	Gault, *Compt. rend.* **148**, 1113 (1909).
Ibid.	Distillation	*Ibid.*, in quantitative yields	Dickens, Kon and Thorpe, *J. Chem. Soc.* **121**, 1501 (1922).
$C_2H_5O_2C-CH(CH_2-CH_2-CO_2C_2H_5)-E$	Distillation, or at 200° *in vacuo*	Triethyl butane-α,δ,δ-tricarboxylate	Dobson, Ferns and Perkin, Jr., *ibid.*, **95**, 2010 (1909). Wislicenus and Schwanhauser, *Ann.* **297**, 110 (1897).
	110-115° and 14 mm.	Ethyl $\Delta^{1,3}$-dihydrosalicylate	Kötz and Grethe, *J. prakt. Chem.* **80**, 509 (1909).

gas is not carbon monoxide. Another keto ester which has little or no tendency to lose carbon monoxide is trimethyl oxydigitogenate, which is thought to have the structure,[122] $C_{16}H_{26}O_7$ $\left\{\begin{array}{l}\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3\\ \text{CH}<\\ \text{CH}<\\ \text{CH}_2\text{—CO}_2\text{CH}_3\end{array}\right.$ $\begin{array}{l}\\ \text{CH—CO—CO}_2\text{CH}_3\\ \\ \\ \end{array}$.

This splits off one molecule of methanol by vacuum distillation and goes into an enol lactone. However, at 275°, the original ester evolves 60 percent of one mol of carbon monoxide.

β-Keto Esters.

One of the characteristic reactions of β-ketonic *acids* is decarboxylation, but the corresponding *esters* show little or no tendency for this type of decomposition. Ethyl acetoacetate is one of the few β-keto esters to have been thoroughly investigated, but its decomposition into dehydroacetic acid indicates that two molecules react with the elimination of two molecules of alcohol:



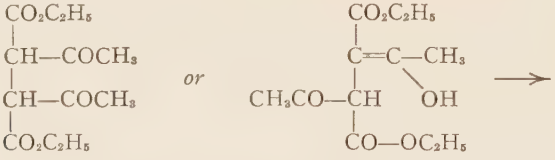
This reaction occurs to a slight extent [123] during an ordinary distillation (boiling point 181°), or by long refluxing, or by passing through a hot pumice-filled tube. By using a special form of reflux condenser which removes the alcohol vapors as fast as formed,[124] a very good yield of dehydroacetic acid may be obtained. Arndt and Nachtwey used a 500 cc. flask attached to a 30 cm. air reflux condenser, which in turn was attached to an ordinary glass-bead fractionating column. From 300 grams of ethyl acetoacetate, 80 grams of which was recovered, they isolated 122 grams of dehydroacetic acid and 68 grams of alcohol.

α,γ-Dibromoacetoacetic ester (p. 551) does not undergo this type of reaction because it is far simpler for it to eliminate ethyl bromide in the manner of γ-bromo esters.

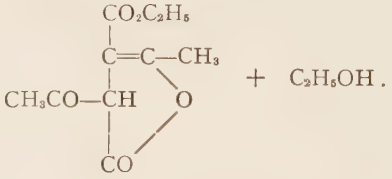
[122] Windaus and Willerding, *Z. physiol. Chem.* **143**, 33 (1925).
[123] Geuther, *Z. Chem.* **1866**, 8. Oppenheim and Precht, *Ber.* **9**, 323 (1876).
[124] Arndt and Nachtwey, *Ber.* **57**, 1489 (1924).

γ- AND δ-KETO ESTERS.

Ethyl diacetosuccinate is both a β- and a γ-keto ester, so therefore it affords a good means of comparing the relative reactivity of the β- and γ-carbonyls. Nothing occurs at the β-position, but a ring closure occurs [125] at the γ-carbonyl, which is functioning as an enol:



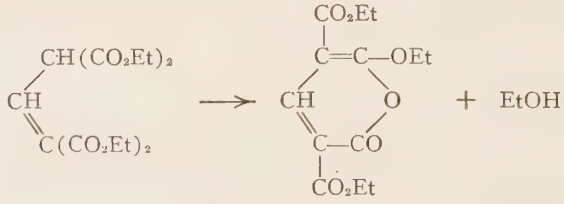
Ethyl diacetosuccinate



isocarbopyrotritaric ester

The enol modification of *o*-carbethoxyphenyl fluorenyl ketone [126] changes into the keto isomer by heating at 220°, or more simply by heating with alcohol. Both of these forms change by heating above 220°, by distillation in a vacuum, into phthalylfluorene.

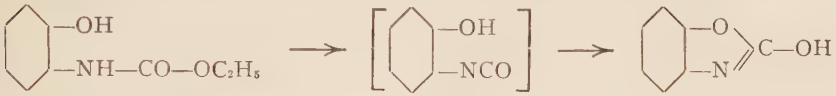
Ethyl dicarbethoxy-glutaconate breaks down [127] in 70 percent yields to ethoxy-pyrone dicarboxylic ester during vacuum distillation (200°), but the homologs may be distilled in a vacuum without pyrolytic changes.



[125] Knorr and Haber, *Ber.* **27**, 1157 (1894).
[126] Wislicenus and Neber, *Ann.* **418**, 274 (1919).
[127] Guthzeit and Dressel, *Ber.* **22**, 1415 (1889).

Hydroxy Esters.

If ethyl lactate is maintained [128] for 7-8 hours at 250°, lactide is produced, and also ethyl lactyl-lactate, CH_3—CHOH—CO—O—$CH(CH_3)$—$CO_2C_2H_5$. Esters of salicylic acid have already been treated. Ethyl alcohol is eliminated [129] from *o*-hydroxyphenyl-urethane at 200°. *o*-Hydroxyphenyl *iso*cyanate may be assumed to be an intermediate product, but the end product, the residue after heating, is oxycarbanil.



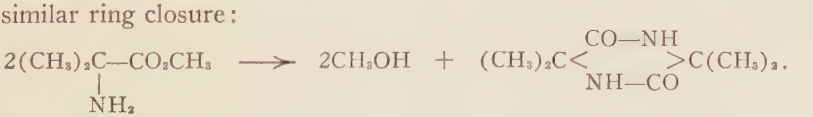
Amino Esters.

α-Amino Esters.

One of the recognized methods of preparation of diketopiperazines consists in heating α-amino esters to 160-180° in a sealed tube. Usually, the change is a very smooth one:

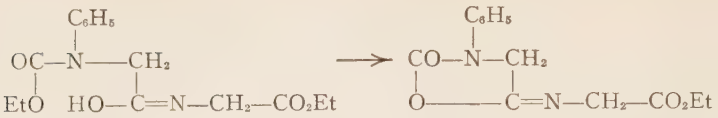
In the simplest case, with methyl aminoacetate, the change occurs [130] even in water solution. The methyl ester of lysine, and of histidine also change at the low temperatures of 100°, but for most esters the favorable temperature is 150-180°. This is true with esters from alanine, phenyl-alanine, leucine, serine, tyrosine, α-aminobutyric acid, and α-amino-*n*-caproic acid.

Earlier (p. 464) it has been pointed out that methyl aminophenylacetate yields diphenyl diketopiperazine when heated in a sealed tube, and that the methyl ester of α-amino*iso*butyric acid (p. 462) undergoes a similar ring closure:



The ethyl ester of the enolic form of carbethoxyl-*N*-phenylglycyl glycine [131] undergoes a complete elimination of one molecule of alcohol in ten minutes at 220°:

[128] Jungfleisch and Godchot, *Compt. rend.* **144**, 425 (1907).
[129] Groenvik, *Bull. soc. chim.* **25**, 177 (1876); *see also* Scott and Mote, *J. Am. Chem. Soc.* **49**, 2546 (1927).
[130] Fischer, *Ber.* **34**, 435 (1901); **39**, 557 (1906); *Ann.* **340**, 126 (1905); Fischer and Suzuki, *Ber.* **38**, 4193 (1905).
[131] Leuchs and Manasse, *Ber.* **40**, 3247 (1907).

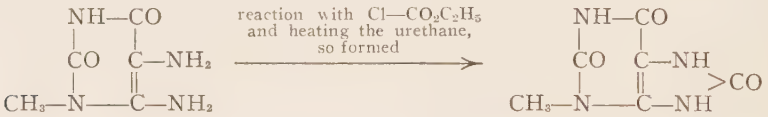


If the methyl ester of lysine, $H_2N—(CH_2)_4—CHNH_2—CO_2CH_3$, is converted into its hydrochloride, and the latter heated [132] to 50°, most of it changes to the dipeptide, lysyl-lysine. This behavior is reasonable, and it is quite in contrast with the formation [133] of ethyl amine (and much ammonia) when the methyl ester of glycine hydrochloride is distilled with dry sodium carbonate:

$$2Cl—NH_3—CH_2—CO_2CH_3 + Na_2CO_3 \longrightarrow 2CH_3CH_2NH_2 + 3CO_2 + 2NaCl + H_2O.$$

Propyl amine is similarly prepared from the ethyl ester.

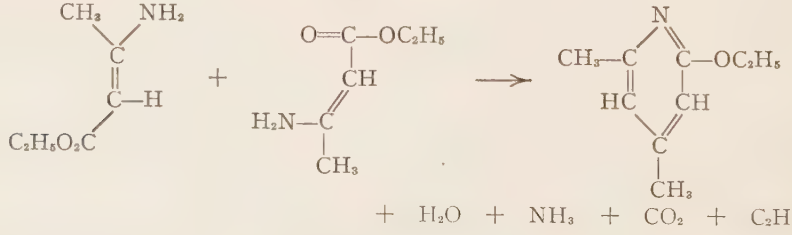
The final step in Traube's synthesis [134] of 3-methyl uric acid from methyl urea and cyanoacetic acid consists in the elimination of alcohol by thermal means from an urethane, derived from 3-methyl-4,5-diamino-2,6-dioxypyrimidine:



This, although not identical, is certainly comparable to the formation of diketopiperazines from α-amino esters.

β-Amino Esters.

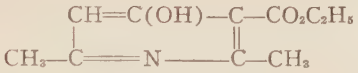
If ethyl aminocrotonate is distilled at ordinary pressure a rather complex decomposition [135] sets in and an ethoxy lutidine, 2,4-dimethyl-6-ethoxypyridine, is produced as the major product. The following equation is given to express this fact:



$$+ H_2O + NH_3 + CO_2 + C_2H_4.$$

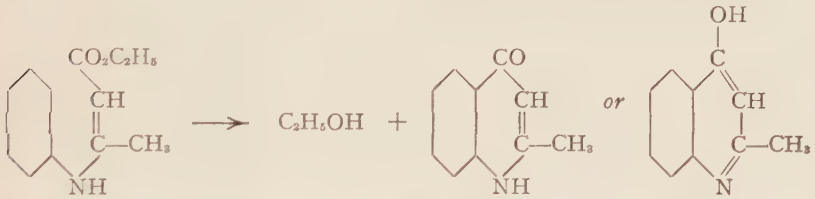
[132] Fischer and Suzuki, *Ber.* **38**, 4182 (1905).
[133] Curtius and Göbel, *J. prakt. Chem.* [2] **37**, 163 (1888).
[134] Traube, *Ber.* **33**, 3041 (1900).
[135] Collie, *J. Chem. Soc.* **67**, 220 (1895).

Another product which has been identified in this reaction is ethyl 4-hydroxy-2,6-dimethyl-pyridine-(3)-carboxylate,[136]

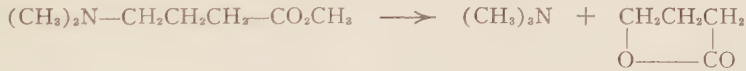


which is formed as alcohol and ammonia are eliminated.

Ethyl anilino-crotonate is analogous to ethyl aminocrotonate but differs somewhat in its mode of pyrolysis because of the presence of the aromatic nucleus. The ethoxyl of the ester becomes liberated as ethyl alcohol by accepting a hydrogen from the aromatic nucleus. γ-Oxyquinaldine is thus formed in fair yields [137] by quick heating to 240°:

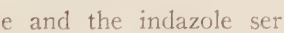


Methyl γ-dimethylamino-butyrate,[138] an illustration of a γ-amino ester, changes at 205° into trimethylamine and butyrolactone:

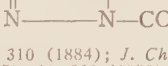


N-Heterocyclic Esters.

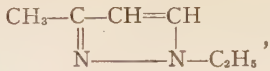
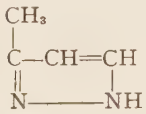
In the pyrazole and the indazole series, von Auwers has made fruitful use of pyrogenic methods to induce the following type of scission:

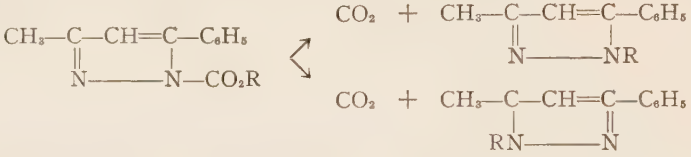


Reference has already been made to the production of amines from α-amino-ester hydrochlorides when distilled with sodium carbonate (p. 562). This might be considered analogous, but it differs in that soda is not used, and it differs also in that the $-CO_2R$ group is directly attached to nitrogen. In other words, von Auwers' compounds are structurally more related to urethanes than to α-amino esters.

In two hours' heating at 140° and 23 mm., the ethyl ester of 3-methyl-*N*-pyrazole carboxylic acid,  , changes [139] into

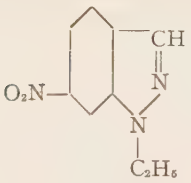
[136] Collie, *loc. cit.; also,* Collie, *Ann.* **226**, 310 (1884); *J. Chem. Soc.* **59**, 174 (1891).
[137] Conrad and Limpach, *Ber.* **20**, 944 (1887); **21**, 523 (1888); **24**, 2990 (1891).
[138] Willstätter, *Ber.* **35**, 617 (1902).
[139] von Auwers and Daniel, *J. prakt. Chem.* **110**, 253 (1925).

a mixture of 1-ethyl-3-methyl pyrazole,  , and 3-methyl pyrazole,  . Carbon dioxide is also liberated from either the methyl- (or the ethyl-) ester of 3,5-methyl-phenyl-*N*-pyrazole carboxylic acid [140] at 180-200° and 200 mm. Two isomeric 1,3,5-trisubstituted pyrazoles result. This fact indicates two concurrent reactions:



Two grams of the original ester was found to yield 1.5 grams of the picrate of the product of the first reaction and 0.3 gram of the picrate of the product of the second reaction.

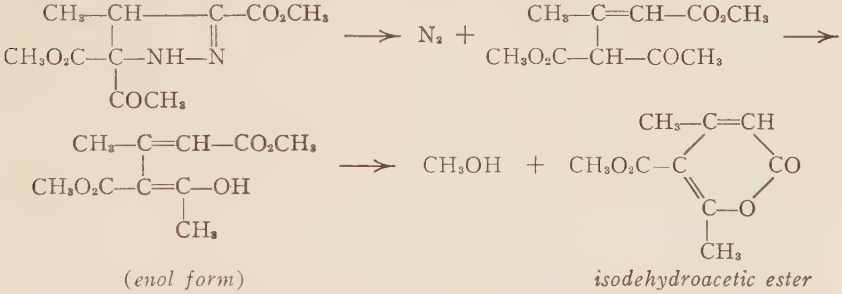
Most esters of indazole-1-carboxylic acid, when heated under suitable conditions, lose carbon dioxide thereby producing both 1- and 2-alkyl indazoles. Resinous matter is also formed. Thus, ethyl indazole-2-carboxylate gives a mixture [141] of 2- and 1-ethyl indazoles. The methyl ester (at 240° and 225 mm. pressure) gives only a small amount of 2-methyl indazole, but the benzyl ester furnishes a 76 percent yield of 2- and 1-benzyl indazole. When dimethyl indazole-1,3-dicarboxylate [142] is distilled (150-180° and 12 mm. pressure), 1-methyl-indazole-3-methylcarboxylate is formed, apparently quite free from the 2-methyl isomer:

The *N*-carbethoxy homolog decomposes similarly at 200-215°. Some alkali-insoluble material, thought to be *N*-ethyl-6-nitroindazole,  (or an isomer), results from the pyrolysis [143] of

[140] von Auwers and Stuhlmann, *Ber.* **59**, 1046 (1926).
[141] von Auwers and Schaich, *Ber.* **54**, 1738 (1921); von Auwers and Lohr, *J. prakt. Chem.* [2] **108**, 300 (1924).
[142] von Auwers and Strödter, *Ber.* **59**, 537 (1926).
[143] von Auwers and Demuth, *Ann.* **451**, 297 (1927).

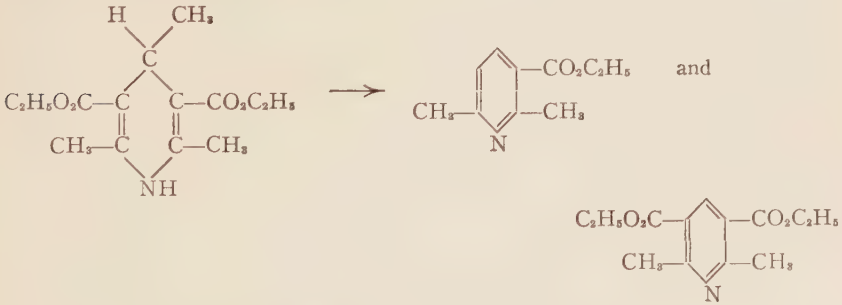
1-carbethoxy-6-nitroindazole (3 hours at 210-215°). 6-Nitroindazole is also in the distillate.

Observe that it is only when the $—CO_2R$ group is attached to nitrogen that carbon dioxide is eliminated in this manner. In one of the illustrations just cited, a $C—CO_2CH_3$ group remained inert whereas the $N—CO_2CH_3$ group became ruptured. In dimethyl 4-methyl-5-acetylpyrazolin-3,5-dicarboxylate no carbomethoxyl groups are attached to nitrogen. This compound does not liberate carbon dioxide when heated, but instead [144] it decomposes above its melting point (85°) into nitrogen and *iso*dehydroacetic ester. It is considered to pyrolyze in two steps:



(enol form) *isodehydroacetic ester*

Symmetrical dihydrocollidine dicarboxylic ethyl ester [145] undergoes pyrolysis into methane, ethylene, oxides of carbon, and into lutidine mono- and di-carboxylic ester:



See pages 707-8 for the behavior of sulfonate esters.

[144] Buchner and Schroeder, *Ber.* **35**, 790 (1902).
[145] Guareschi and Grande, *Chem. Zentr.* **1889**, II, 440.

CHAPTER 18.

ACID CHLORIDES AND ACID ANHYDRIDES.

Acid Chlorides.

Formyl Chloride.

The simplest acid chloride, formyl chloride, is non-existent[1] above −20°. Its mode of decomposition into carbon monoxide and hydrogen chloride:

$$H{-}COCl \longrightarrow CO + HCl,$$

is illustrative of the tendency of many other acid chlorides to eliminate carbon monoxide. Such a tendency has a counterpart in the tendency of diazonium chlorides to eliminate nitrogen. The resemblance between carbon monoxide and nitrogen is far more than a superficial one. Both molecules possess ten valence electrons, and both are comparatively inert. Lewis[2] has pointed out that both may have the same type of formula, namely, :N:::N: and :C:::O:. Nitrogen is, of course, the more stable of the two, and presumably, therefore, its tendency to become free nitrogen would be greater than that of the carbonyl group to appear as carbon monoxide. A consideration of the following two series of compounds emphasizes this statement.

$\left[\begin{matrix}H{-}C{-}Cl\\ \quad\|\\ \quad O\end{matrix}\right]$	unstable at −20°;	$\left[\begin{matrix}H{-}N{-}Cl\\ \quad\|\|\|\\ \quad N\end{matrix}\right]$	unknown
$\begin{matrix}H{-}C{-}OH\\ \quad\|\\ \quad O\end{matrix}$	unstable at 150°;	$\left[\begin{matrix}H{-}N{-}OH\\ \quad\|\|\|\\ \quad N\end{matrix}\right]$	unknown
$\begin{matrix}R{-}C{-}Cl\\ \quad\|\\ \quad O\end{matrix}$	stable;	$\left[\begin{matrix}R{-}N{-}Cl\\ \quad\|\|\|\\ \quad N\end{matrix}\right]$	unknown
$\begin{matrix}Ar{-}C{-}Cl\\ \quad\|\\ \quad O\end{matrix}$	stable;	$\begin{matrix}Ar{-}N{-}Cl\\ \quad\|\|\|\\ \quad N\end{matrix}$	unstable

Acetyl Chloride.

Acetyl chloride becomes pyrolyzed by a hot (700-850°) platinum wire into ethylene, hydrogen chloride and carbon monoxide. To explain it, Joist and Loeb[3] assumed a methylene dissociation:

[1] Nef, *J. Am. Chem. Soc.* **26**, 1558 (1904).
[2] Lewis, "Valence, and the Structure of Atoms and Molecules," New York, The Chemical Catalog Co. 1923, p. 127.
[3] Joist and Loeb, *Z. Elektrochem.* **11**, 938 (1905).

$$2CH_3COCl \longrightarrow 2[CH_2<] + 2[HCOCl]$$
$$\downarrow \qquad\qquad \downarrow$$
$$C_2H_4 \qquad 2HCl + 2CO.$$

A more straightforward reaction methanism is one which assumes carbon monoxide and methyl chloride as the intermediate step. It has been shown that methyl chloride is appreciably decomposed at 500°:

$$CH_3COCl \longrightarrow CH_3Cl + CO, \text{ and } 2CH_3Cl \longrightarrow C_2H_4 + 2HCl.$$

Still another reaction mechanism is to assume the decomposition into ketene and hydrogen chloride, a reaction which is known to be reversible at lower temperatures. If this is the correct reaction mechanism, it explains the presence of any "undecomposed acetyl chloride". The equation would be:

$$CH_3COCl \rightleftharpoons CH_2{=}C{=}O + HCl.$$

There is good indirect evidence to support both of these latter two reaction mechanisms. Triphenylacetyl chloride, which offers no opportunity for the elimination of hydrogen chloride, decomposes with surprising ease [4] into carbon monoxide and triphenyl-chloro-methane:

$$(C_6H_5)_3C{-}CO{-}Cl \longrightarrow (C_6H_5)_3C{-}Cl + CO.$$

This reaction starts at the melting point, and is quantitatively completed at 180°. Palmityl chloride, on the other hand, when heated [5] in carbon dioxide for 4 hours at 210-275°, gives off hydrogen chloride quantitatively and leaves a residue of what is presumably tristetradecyl ketene:

$$3C_{15}H_{31}{-}COCl \longrightarrow 3HCl + (C_{14}H_{30}{-}CH{-}CO)_3.$$
$$\qquad\qquad\qquad

$$(C_6H_5)_2CH{-}COCl \begin{cases} \longrightarrow HCl + (C_6H_5)_2C{=}C{=}O \\ \longrightarrow CO + [(C_6H_5)_2CHCl] \longrightarrow HCl + \tfrac{1}{2}(C_6H_5)_2C{=}C(C_6H_5)_2 \end{cases}$$

In the preparation [7] of diphenyl-chloro-acetyl chloride, $(C_6H_5)_2CCl{-}COCl$, distillation, even at low pressures, cannot be employed as a method of purification. Bistrzycki and Landtwing showed that between 200-280° both carbon monoxide and hydrogen chloride were eliminated in nearly the theoretical amounts. To appreciate the course of this reaction in which hydrogen chloride is eliminated, it is helpful to learn that diphenyl-*p*-tolyl-acetyl chloride, $CH_3C_6H_4{-}C(C_6H_5)_2{-}COCl$, loses carbon monoxide quantitatively at 120° (giving Ar_3CCl), but that at 200° hydrogen chloride is also quantitatively expelled. Bistrzycki infers that *ms-p*-tolyl fluorene constitutes the major portion of the residue, without definite evidence, however, in support of the contention. In view of the fact that triphenylchloromethane changes into 9-phenyl fluorene (p. 138) at 200°, the assertion is very reasonable. Thus:

$$(C_6H_5)_2C{<}\begin{matrix}Ar\\Cl\end{matrix} \longrightarrow HCl + (C_6H_4)_2C{<}\begin{matrix}Ar\\H\end{matrix}$$

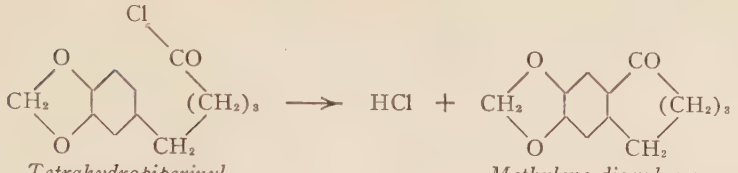
α,α-Di-*p*-tolyl-propionyl chloride is fairly stable at 115°, but carbon monoxide is evolved stormily at 180°. If the substance is maintained at 220° for a considerable time, the hydrogen chloride is also completely liberated leaving ditolyl ethylene in the residue:

$$(CH_3C_6H_4)_2C(CH_3){-}COCl \longrightarrow (CH_3C_6H_4)_2C(CH_3){-}Cl \longrightarrow (CH_3C_6H_4)_2C{=}CH_2.$$

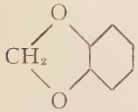
Both carbon monoxide and hydrogen chloride are also evolved [8] by heating α-*p*-tolyl-*iso*butyryl chloride, $(CH_3)_2C(C_6H_4CH_3){-}COCl$.

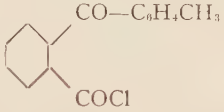
The chloride of tetrahydropiperinic acid undergoes a ring closure by distillation. Borsche and Eberlein [9] considered this to be a thermal effect, although their method was to distil [boiling point (16 mm.) 200-215°] the reaction mixture of phosphorus trichloride with the acid. From 22 grams of the acid, there was collected 12 grams of the cyclic ketone. Since thionyl chloride could be substituted for phosphorus trichloride, the phosphorus compounds which were present during the distillation were thought to play no rôle.

[7] Staudinger, *Ann.* **356**, 72 (1907).
[8] Bistrzycki and Landtwing, *Ber.* **42**, 4721 (1909).
[9] Borsche and Eberlein, *Ber.* **47**, 1460 (1914).



Tetrahydropiperinyl chloride *Methylene dioxybenzo-suberone*

A similar reaction, giving the cyclic hexanone, takes place with the corresponding butyric derivative; and from the propionic derivative,  , hydrogen chloride is also eliminated, thereby yielding 4,5-methylenedioxy-α-hydrindone.

2-(*p*-Toluyl)-benzoyl chloride,[10]  , loses hydrogen chloride between 110-190°, and more rapidly if a vacuum is employed. The reaction mass still gives tests for chlorine, but Limpricht and Wiegand considered it to be largely composed of a compound with 45 carbons, and another with 60 carbons, in the molecule. Fifteen carbons are in the original substance.

Acetanilide-imide-chloride, $C_6H_5—N=C<^{CH_3}_{Cl}$, possesses a structural similarity to acetyl chloride, $O=C<^{CH_3}_{Cl}$, but the former shows a tendency to polymerize,[11] not found in the latter, when warmed above 50°. It yields a dimer, $C_6H_5N=C(CH_3)—CH_2—CCl=NC_6H_5.HCl$. (See p. 585.)

PHOSGENE (CARBONYL CHLORIDE).

The kinetics of the decomposition of carbonyl chloride have received rather careful study by several investigators. At 800°, there is a complete change[12] into carbon monoxide and chloride:

$$COCl_2 \longrightarrow CO + Cl_2,$$

and at 503° the equilibrium value reaches a 67 percent dissociation. For the range 349-452°, Bodenstein[13] believes that the velocity and the equilibrium are to be represented by three reactions:

[10] Limpricht and Wiegand, *Ann.* **311**, 184 (1900).
[11] Wallach, *Ann.* **184**, 93 (1877); **214**, 193 (1882).
[12] Bodenstein and Dunant, *Z. physik. Chem.* **61**, 437 (1908).
[13] Bodenstein and Plaut, *ibid.* **110**, 339 (1924).

$$(1) \quad Cl_2 \rightleftharpoons 2Cl$$

$$(2) \quad Cl + Cl_2 \rightleftharpoons Cl_3$$

$$(3) \quad Cl_3 + CO \rightleftharpoons COCl_2 + Cl,$$

and he points out that side reactions in the first two equations are continuous equilibria which fix the velocity x of the third reaction. Calculations show that the second reaction consumes 51,400 calories, and that its state of equilibrium conforms to the Nernst heat principle.

Stock and Wustrow [14] report a 52 percent conversion of phosgene at 500° (2 hours) into carbon monoxide and chlorine, and a 0.7 percent disproportionation into carbon dioxide and carbon tetrachloride. Calculations by Nernst would lead one to expect a nearly complete decomposition between 200-800°, but this value is not approached in practice. Between 432-472°, the velocity (h) of the pyrolysis of phosgene is given [15] by the expression,

$$h = k\sqrt{C_{Cl_2}}\left(C_{COCl_2} - \frac{C_{CO} \cdot C_{Cl_2}}{K}\right),$$

where k is a constant, and K is the equilibrium constant of the decomposition of carbonyl chloride. This equation holds only if the concentrations of carbon monoxide, chlorine and carbonyl chloride are of the same order of magnitude (10^{-3} to 10^{-4} mols per liter), or if sufficient time has elapsed from the beginning of the reaction. The velocity is uninfluenced by air or by the relative glass surface. On the assumption that the expression for the velocity of the decomposition does not change with the temperature, then

$$\log k = -\frac{11420}{T} + 15.154,$$

between 685-782° (absolute temperature).

Still more recently, Ingleson [16] has studied the constants of the thermal decomposition of carbonyl chloride. At 357° C., he finds K_c, the dissociation constant, to be 3654; at 415°, 717.9; at 444.1°, 348.2; and at 481.4°, 151.6. A plot of log $K_c/100$ against the reciprocal of the corresponding absolute temperature (between 357° C. and 481.4° C.) shows the points to lie on a straight line. Ingleson believes that the reaction products of the decomposition catalyze the decomposition. Furthermore, for accurate work, he points out that quartz apparatus should be used instead of glass. The percentage of decomposition of the phosgene at 357° is 11-12 percent; at 415°, 27-28 percent; at 444.1°, 39-40 percent; and at 481.4°, 52-55 percent.

[14] Stock and Wustrow, *Z. anorg. allgem. Chem.* **147**, 245 (1925).
[15] Christiansen, *Z. physik. Chem.* **103**, 99 (1922).
[16] Ingleson, *J. Chem. Soc.* **1927**, 2244. For carbonyl bromide, see Lenher and Schumacher, *Z. physik. Chem.* **135**, 85 (1928).

A table containing the values of the dissociation constants of phosgene (the values of many workers included) at temperatures from 341° to 603° is given by Dyson in *Chemical Reviews* **4**, 123 (1927).

Oxalyl Chloride.

Oxalyl chloride [17] undergoes a quantitative pyrogenic reaction into carbon monoxide and phosgene, by passing it through a glass tube (1 meter long) at 600°, although at 200° it is unchanged:

$$Cl—CO—CO—Cl \longrightarrow COCl_2 + CO$$

Oxalic acid-half chloride, HO—CO—CO—Cl, is short-lived.[18] It soon breaks down into carbon dioxide, carbon monoxide and hydrogen chloride. The ester of this half-chloride, ethoxalyl chloride (see p. 549 for its preparation by methods of pyrolysis), suffers decomposition [19] by passing it through a tube at 200° into carbon monoxide and ethyl chlorocarbonate:

$$Cl—CO—CO_2C_2H_5 \longrightarrow CO + Cl—CO_2C_2H_5$$

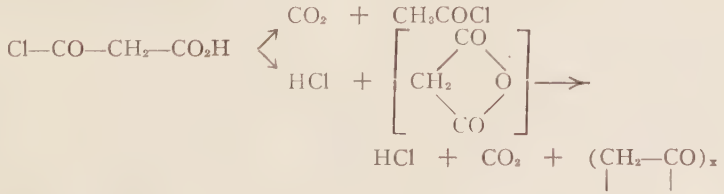
Other Acid Chlorides.

Carbon monoxide is quantitatively liberated [20] during the preparation of *p*-dimethylaminophenyl-glyoxylyl chloride unless good cooling is maintained:

$$(CH_3)_2N—C_6H_4—CO—COCl \longrightarrow (CH_3)_2N—C_6H_4—COCl + CO$$

Oxanilic acid chloride,[21] $C_6H_5NH—CO—COCl$, melts at 82.5°. Above this temperature it evolves gases and changes into phenyl *iso*cyanate, carbon monoxide and hydrogen chloride. Aschan recommends this as a means of preparation of *phenyl-isocyanate*. The yields are high.

Two types of decomposition [22] are met in the half chloride of malonic acid when heated above its melting point, 65°. In one, the carboxyl group is eliminated as carbon dioxide, and in the other type, hydrogen chloride and carbon dioxide are liberated, accompanied by the formation of a resinous polymer of ketene.



[17] Staudinger, *Ber.* **41**, 3565 (1908).
[18] Gerhardt, *Ann. chim.* [3] **37**, 293 (1853); *Ann.* **87**, 67 (1853).
[19] Grassi, *Gazz. chim. ital.* **27**, I, 32 (1897).
[20] Staudinger and Stockman, *Ber.* **42**, 3486 (1909).
[21] Aschan, *Ber.* **23**, 1823 (1890).
[22] Staudinger and Ott, *Ber.* **41**, 2208 (1908).

Ketene, as such, has not been isolated in the above reaction, but dimethyl ketene and diethyl ketene are prepared by this method:

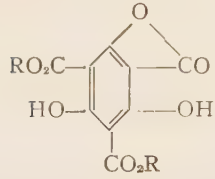
$$R_2C\begin{matrix}CO_2H\\COCl\end{matrix} \longrightarrow HCl + R_2C\begin{matrix}CO\\CO\end{matrix}>O \text{ (isolable).}$$

Diethyl malonic anhydride, prepared in this manner, decomposes at 160-180° and 9 mm. smoothly into diethyl ketene:

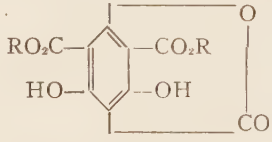
$$R_2C\begin{matrix}CO\\CO\end{matrix}>O \longrightarrow R_2C{=}C{=}O + CO_2.$$

In this case, the decomposition into $(C_2H_5)_2CH{-}COCl + CO_2$ is a minor one.

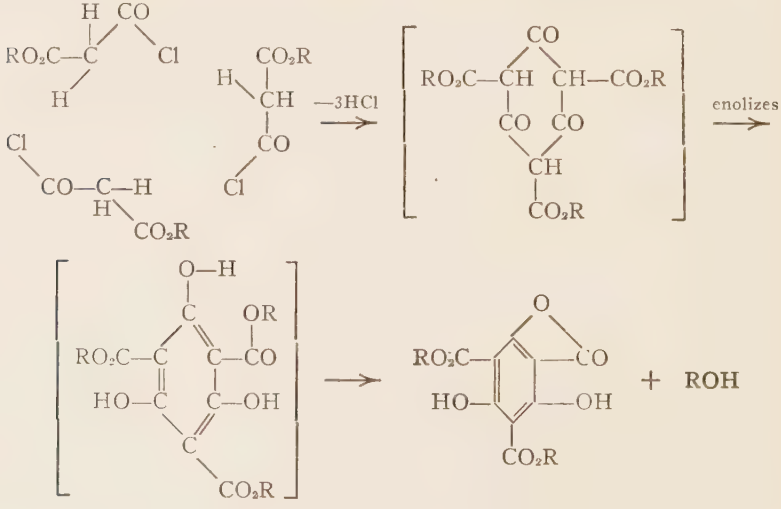
In a study of the decomposition [23] at 125-130° of malonyl chloride monoethyl ester (or the monomethyl ester), Leuchs reported a 10 percent yield of a red substance which, by loss of ethyl chloride and carbon monoxide, may be a resinous polymer of ketene $(CH_2CO)_x$. There was also a 4 percent yield of an ester, with one of two alternative structures:



or



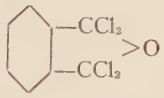
This results by elimination of three molecules of hydrogen chloride from three of the chloride-ester, probably in the following manner.



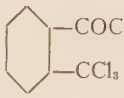
[23] Leuchs, *Ber.* **39**, 2641 (1906).

If succinyl chloride monethyl ester, $Cl—CO—CH_2—CH_2—CO_2C_2H_5$, is distilled at as high a pressure as 42 mm. (115°), there occurs [24] a partial decomposition into ethyl chloride and succinic anhydride, and a lesser change into ethyl succinate and succinyl chloride.

An equilibrium value is reached by heating either the high-melting or the low-melting forms of phthalic acid chlorides.[25] There are genuine structural differences in these two compounds; the former is



and the latter,



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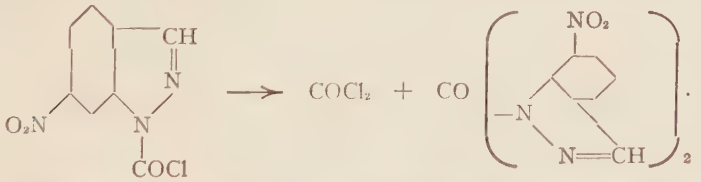
Ring closure, by the elimination of methyl chloride, features the change of carbomethoxyl-glycyl chloride at 70°:

The yield for this transformation is 70 percent, but only 30 percent yield is attained when the carbethoxyl derivative [26] is employed.

The change of a "carbamyl chloride" into an urea derivative by the elimination of phosgene is exemplified [27] in the decomposition of 6-nitro-indazole-1-carboxylyl chloride above its melting point, 140°. 6,6′-Dinitro-carbonic acid-1,1′-diindazylide is formed.



Carbamyl chloride, itself, is a colorless liquid [28] that fumes in the air and commences to distil at 60° with much decomposition into *iso*cyanic acid and hydrogen chloride:

(see p. 606). Compounds related to carbamyl chloride such as phenylcarbamyl chloride also pyrolyze in this manner, yielding *iso*cyanates. The first mention that phosgene might be used in this connection to convert aniline hydrochloride or carbanilide into phenylcarbamyl chlo-

[24] Michaelis and Hermans, *Ber.* **25**, 2749 (1892); Blaise, *Bull. soc. chim.* [3] **21**, 647 (1899).
[25] Ott, *Ber.* **55**, 2108 (1922).
[26] Leuchs, *Ber.* **39**, 857 (1906); Leuchs and Geiger, *Ber.* **41**, 1725 (1908).
[27] von Auwers and Demuth, *Ann.* **451**, 301 (1927).
[28] Gattermann and Schmidt, *Ber.* **20**, 858 (1887); Dyson, *Chem. Reviews* **4**, 135 (1927).

ride [29] was made by Hentschel, a method which was later patented by Hofmann and Schoetensack:

$$C_6H_5NH—CO—Cl \longrightarrow HCl + C_6H_5N{=}C{=}O.$$

With *p*-phenylene diamine [30] it is possible to secure the double *iso*cyanate by heating the hydrochloride of the base to 200-250° in a stream of phosgene. Benzidine also behaves in this manner. The following pyrolysis [31] is of interest in this connection:

An acid chloride, Cl—SO—O—CH_2—COCl, which is formed by the interaction [32] of glycollic acid and thionyl chloride, becomes pyrolyzed at 180° into sulfur dioxide and chloroacetyl chloride.

Acid Anhydrides.

Usually, acid anhydrides [33] are more resistant to heat than the parent acids. To illustrate this, it may be stated that diphenylacetic anhydride,[34] $((C_6H_5)_2CH—CO)_2O$, triphenylacetic anhydride and diphenylchloroacetic anhydride are all stable at 250-300° whereas the free acids lose carbon dioxide at a lower temperature. Formic acid and malonic acid may be cited as exceptional cases since their anhydrides are unknown. Carbon monoxide and carbon suboxide, the dehydration products of these acids, are not their acid anhydrides but their ketenes, inasmuch as one molecule of water has been eliminated for each carbonyl group. This is made more obvious by a comparison of the relationship of acetic acid, acetic anhydride and ketene:

$$2CH_3—CO_2H \quad ; \quad (CH_3CO)_2O \quad ; \quad 2CH_2{=}C{=}O. \quad \text{(See p. 334.)}$$

Acetic Anhydride.

Acetic anhydride is known to give ketene [35] by subjecting it to the action of a hot platinum coil. This was the method which led to its discovery. In this method, a coiled platinum wire (50×0.2 mm.) is placed beneath a 50 gram charge of pure acetic anhydride. Seven amperes suffices at the start, but gradually the amperage must be raised to 12 or 14, because of carbon coating. About 15-20 cc. of liquefied

[29] Hentschel, *Ber.* **17**, 1284 (1884); Hofmann and Schoetensack, D.R.P., 29,929.
[30] Gattermann and Wramplemeyer, *Ber.* **18**, 2604 (1885); Snape, *J. Chem. Soc.* **49**, 255 (1886).
[31] Loeb, *Ber.* **18**, 2427 (1885).
[32] Blaise and Montagne, *Compt. rend.* **174**, 1173 (1922).
[33] Staudinger, *Ber.* **44**, 544 footnote (1911).
[34] See p. 579 for its behavior in a vacuum at 220°.
[35] Wilsmore, *J. Chem. Soc.* **91**, 1938 (1907); Deakin and Wilsmore, *ibid.* **97**, 1968 (1910).

ketene can be produced by this method, which obviously is inferior to the acetone method (p. 249).

Ketene may also be prepared from acetic anhydride [36] by the usual method of passing its vapors through a hot tube. In Peytral's method, a short platinum tube is heated to 1150°, at which temperature it is necessary to provide a rapid flow of the anhydride vapors to prevent undue decomposition of the ketene:

$$(CH_3CO)_2O \rightleftharpoons \begin{matrix} CH_3CO_2H \\ \downarrow \\ CH_4 + CO_2 \end{matrix} + \begin{matrix} CH_2{=}C{=}O \\ \downarrow \\ \tfrac{1}{2}C_2H_4 + CO \end{matrix} .$$

Some of the ethylene (see equation) suffers further pyrolysis into hydrogen and acetylene (p. 56). Ketene may have been formed in Nef's experiment [37] with acetic anhydride. He passed 65.4 grams of the anhydride over pumice at 580° during 45 minutes and obtained 5.5 liters of gas (63.5 percent carbon monoxide; 24.3 percent methane; 12.2 percent hydrogen), 45 grams of liquid (some acetic acid, but largely acetic anhydride), and ethylene (3 grams of ethylene bromide). Heating acetic anhydride [38] at 300° for 3 hours changes it into acetone and carbon dioxide. This is accompanied by a little charring. In 7 hours, there is also produced a little acetylacetone. Since acetone may be produced in this manner, and since ketene may be produced from acetone, it suggests that acetone is the intermediate compound in the transformation from acetic anhydride to ketene:

$$(CH_3CO)_2O \longrightarrow CH_3COCH_3 + CO_2 .$$

Mixed Anhydrides.

The common acid anhydrides are the symmetrical ones. The unsymmetrical, or mixed, acid anhydrides possess but little of the stability shown by the symmetrical members. The tendency is for a disproportionation [39] to the two symmetrical forms:

$$2R{-}CO{-}O{-}COCH_3 \longrightarrow (RCO)_2O + (CH_3CO)_2O .$$

Possibly their instability has been somewhat overemphasized, for acetic *iso*valeric anhydride may be distilled [40] without much decomposition, and even after several hours' refluxing it is not completely decomposed. Mixed anhydrides such as acetic-propionic and acetic-*iso*butyric may also be prepared, but with the higher fatty acids (palmitic or stearic),

[36] Peytral, *Bull. soc. chim.* **35**, 969 (1924).
[37] Nef, *Ann.* **318**, 222 (1901).
[38] Bamberger, *Ber.* **43**, 3517 (1910).
[39] Autenrieth, *Ber.* **34**, 168 (1901).
[40] Autenrieth and Thomae, *Ber.* **57**, 423 (1924).

only the simple anhydrides are obtained. Formic acetic anhydride is known, and may be distilled in a vacuum, but at atmospheric pressure it decomposes [41] as it boils (105-120°).

Acetyl chloride and the dry sodium salts of benzoic, *p*-toluic, or cinnamic acids react to form viscid oils which on attempted distillation [40] *in vacuo* give good yields of acetic anhydride and the anhydride of the aromatic acid. If these oils are really mixed anhydrides they must undergo disproportionation at room temperature, for with aniline in the cold, they give a mixture of the two theoretically possible anilides.

Mixed phenylcarbamic anhydrides,[42] R—CO—O—CO—NHC_6H_5, are fairly stable at ordinary temperatures when *R—CO—* represents benzoyl or cinnamyl. At about 100°, these decompose into the acid anhydride and symmetrical diphenyl urea, and at 160° these substances react yielding the anilides and carbon dioxide. When *R—CO—* represents acetyl or phenylacetyl, the anilides are formed at ordinary temperature.

Acetyl nitrates,[43] CH_3—CO—O—NO_2, a mixed anhydride prepared by the interaction of acetic and nitric anhydrides on the cold, is a colorless fuming liquid which explodes violently when suddenly heated at ordinary pressure. At 70 mm., it boils at 22°. Thionyl benzoate, a benzoyl derivative of an inorganic acid, breaks down almost spontaneously [44] into benzoic anhydride and sulfur dioxide:

$$(C_6H_5CO{-}O)_2SO \longrightarrow (C_6H_5CO)_2O + SO_2.$$

p-Nitrobenzoyl oxalic anhydride melts with decomposition [45] at 169°, in accordance with the general equation:

$$\begin{array}{l} Ar{-}CO_2{-}CO \\ \quad\quad\quad | \\ Ar{-}CO_2{-}CO \end{array} \longrightarrow (ArCO)_2O + CO_2 + CO.$$

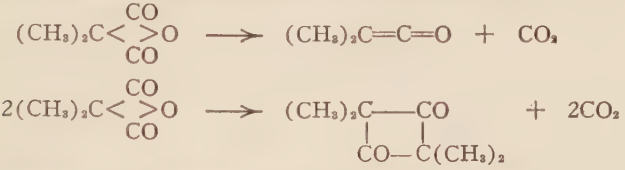
When Ar represents *m*-nitrobenzoyl, 3,5- or 2,4-dinitrobenzoyl the pyrolysis occurs in the usual way, but when Ar represents 2,4,6-trinitrobenzoyl, trinitrobenzene is the compound which is formed. The decomposition in the latter instance occurs at 228°.

Substituted Malonic Anhydrides, and Ketenes.

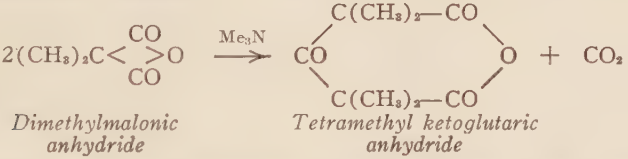
Previously (p. 572), reference has been made to the stability of disubstituted malonic anhydrides, as well as of their pyrolysis at mod-

[41] Behal, *Compt. rend.* **128**, 1460 (1899); *Ann. chim.* [7] **20**, 418 (1900).
[42] Dieckmann and Breest, *Ber.* **39**, 3052 (1906).
[43] Pictet and Khotinsky, *Compt. rend.* **144**, 210 (1907).
[44] Denham and Woodhouse, *J. Chem. Soc.* **103**, 1864, 1868 (1913).
[45] Adams and Ulich, *J. Am. Chem. Soc.* **42**, 599 (1920); Adams, Wirth and French, *ibid.* **40**, 424 (1918).

erately high temperatures into ketenes. In particular, the preparation of diethyl ketene from diethyl-malonic anhydride [46] at 160-180° and 9 mm. was mentioned. Dimethylmalonic anhydride also pyrolyzes in this manner to dimethyl ketene. To prevent polymerization, which takes place quantitatively [47] if the anhydride is heated at 100° in a sealed tube, dimethylmalonic anhydride is heated in an open distilling bulb at 100°, and the escaping dimethyl ketene is cooled at once to —80°.



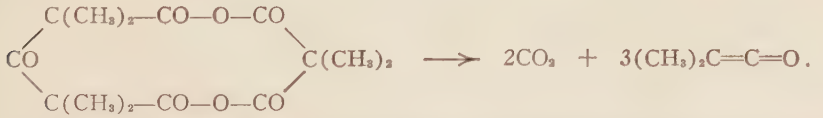
A third reaction (90 percent yield) occurs at 70-80°, if 1 percent of trimethylamine is added:



Dimethylmalonic anhydride — *Tetramethyl ketoglutaric anhydride*

Because of the essential presence of trimethylamine, this change is not a pyrolytic one. It is mentioned here, not only because of its relation to the others, but also because of the fact that further heating of the keto-glutaric anhydride causes its breakdown into dimethyl ketene.

Mixed anhydrides, which can be prepared by the reaction of carbon dioxide and dimethyl ketene at —80° when catalyzed by a small percentage of triethylamine, also decompose above their melting points; thus,



Other addition compounds of dimethyl ketene [48] have also been studied, and for the most part have been found to decompose into the constituent parts at moderate temperatures. To illustrate:

$2(CH_3)_2C{=}C{=}O \cdot 3C_6H_5NCO$		decomposes at	210°
1 " $\cdot$ 4 "		"	225°
3 " $\cdot 2\ \alpha\text{-}C_{10}H_7NCO$		"	250°
3 " $\cdot 2\ p\text{-}O_2N{-}C_6H_4{-}NCO$		"	155°
5 " $\cdot 2COS$		"	110° (partial)
5 " $\cdot 2CS_2$		"	160° (partial)

[46] Staudinger and Ott, *Ber.* **41**, 2208, 3829 (1908).
[47] Staudinger, Felix and Harder, *Helv. Chim. Acta* **8**, 306 (1925).
[48] Staudinger, Felix and Geiger, *Helv. Chim. Acta* **8**, 314 (1925).

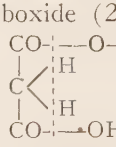
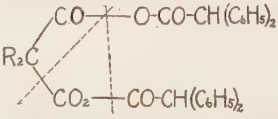
No addition was apparent with CH_3NCO, $CH_3O—C_6H_4NCO$ (*p*), or C_6H_5NCS.

A curious kind of mixed malonic anhydride has also been investigated by Staudinger,[49] and here again, disubstituted ketenes are pyrolytic products. A general equation is:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CO—O—CO \\ CO—O—CO \end{matrix}\!\!>\!C(C_6H_5)_2 \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}CO + 2CO_2 + (C_6H_5)_2C{=}CO$$

TABLE LV. *Pyrolysis of Mixed Malonic Anhydrides.*

R	R′	Conditions	Ketene Formed
Methyl	Ethyl	Heat *in vacuo*	Methyl ethyl ketene
Propyl	Propyl	*Ibid.*	Dipropyl ketene
Benzyl	Benzyl	104°	Dibenzyl ketene (73 percent yield)
Methyl	Benzyl	.....	Methyl benzyl ketene; polymerized after a day's standing
Allyl	Allyl	95°	Diallyl ketene (80 percent yield)
Allyl	Methyl	70°	Allyl methyl ketene
Ethyl	Bromo	Distillation at 15 mm.	Ethyl bromo ketene (9 percent yield)
Ethyl	Phenoxy	*Ibid.*	Ketene not isolated, but its presence demonstrated
Phenoxy	Phenoxy	*Ibid.*	*Ibid.*
Methyl	Ethoxy	Unsuccessful	.....
Ethoxy	Ethoxy	Unsuccessful	.....

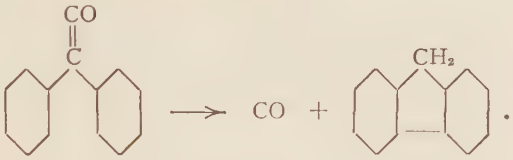
At 100°, malonic acetic anhydride [50] decomposes to form a little carbon suboxide (2 percent yield). Whereas this is possible with the structure,  , it becomes impossible for a mixed anhydride of dialkylmalonic acid. In fact, dimethylmalonic diphenylacetic anhydride [51] breaks down by distilling at 20 mm. into dimethyl ketene (49 percent yield), a polymer of it, diphenylacetic anhydride, and the calculated amount of carbon dioxide. This pyrolysis is in keeping with the other results with dialkylmalonic anhydride. The cleavage planes are evidently:  . Similarly, the diethyl homolog furnishes a 64 percent yield of diethyl ketene. If the temperature of the bath reaches 200-220°, some diphenyl ketene also distils over. This is indicative of the pyrolysis of diphenylacetic anhydride:

$$((C_6H_5)_2CH—CO)_2O \longrightarrow (C_6H_5)_2CH—CO_2H + (C_6H_5)_2C{=}C{=}O.$$

[49] Staudinger and others, *ibid.* **6**, 291 (1923).
[50] Ott, *Ann.* **401**, 159 (1914).
[51] Staudinger, Anthes and Schneider, *Ber.* **46**, 3539 (1913).

The ethyl chloro derivative in the above series pyrolyzes (in a hydrogen atmosphere) into ethyl chloro ketene in 50 percent yields. Ethyl chloro ketene, a liquid, polymerizes in one or two minutes to a white solid.

This discussion relative to ketenes is appropriately placed in the chapter on acid anhydrides, inasmuch as ketenes are "super acid anhydrides". Ketene, itself, is known to pyrolyze at very high temperatures into ethylene and carbon monoxide (see p. 252). Indirect evidence is at hand to show that methyl ketene [52] breaks not only at the double bond but also at the single bond, inasmuch as ketene is one of the pyrolytic products of diethyl ketone, a ketone which should give methyl ketene exclusively as a primary product. According to Staudinger, dimethyl ketene [53] pyrolyzes at high temperatures into carbon monoxide and "*iso*propylidene", the latter appearing as propylene or as tetramethyl ethylene. Diphenyl ketene is less stable towards heat than tetraphenyl ethylene, unsymmetrical diphenyl ethylene, or diphenyl dichloro ethylene, $(C_6H_5)_2C{=}CCl_2$, all of which have somewhat related structures. Staudinger established the fact that if 6 grams of diphenyl ketene is slowly distilled over a silver spiral at 600-700°, there is formed a 2.2 gram yield of fluorene. Presumably, carbon monoxide is the other product, in which case the equation is:

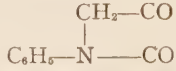


Succinic and Glutaric Anhydrides.

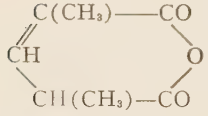
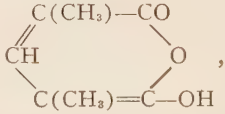
Much is known of the pyrolytic change from succinic or glutaric acids, and related compounds, into their anhydrides, but little is known concerning the further decomposition of these anhydrides. As stated on page 404, succinic anhydride may pyrolyze into carbon dioxide and a three-carbon residue, $—CH_2—CH_2—CO—$, which may then combine with itself or with some undecomposed succinic anhydride. As stated earlier, the dilactone of acetone diacetic acid is the major product. It has been found [54] in the author's laboratory that a 41-42 percent yield of this substance may be obtained from pure succinic anhydride if the latter is heated for 6 hours at 250-280° (reflux).

[52] Hurd and Kocour, *J. Am. Chem. Soc.* **45**, 2167 (1923); Hurd, *ibid.* **45**, 3096 (1923).
[53] Staudinger, "Die Ketene," Stuttgart, F. Enke, 1912, p. 142; Staudinger and Endle, *Ber.* **46**, 1437 (1913).
[54] Hurd and Bennett, unpublished results.

The distillation[55] of ethyl anhydrosuccinate, $O(COCH_2CH_2CO_2Et)_2$, at atmospheric pressure causes carbonization. After 4 distillations, there is produced a mixture of much succinic anhydride and a little ethyl succinate.

N-Carboxyl-*N*-phenylglycine anhydride,[56]  , melts with loss of carbon dioxide, changing into an amorphous substance, melting point 245°, which is probably $(—N(C_6H_5)—CH_2—CO—)_x$.

Almost nothing is known regarding the pyrolysis of glutaric anhydride. The simple glutaric anhydrides are obviously quite stable to heat, and have not been investigated. The thermal decomposition of tetramethyl ketoglutaric anhydride, and related compounds, into dimethyl ketene and carbon dioxide has been expounded on p. 577.

The normal anhydride[57] of α,γ-dimethyl glutaconic acid,  , changes in ten minutes at 150° into the "hydroxy-anhydride", hydroxy-2-dimethyl-3,5-pyrone-6,  , by a process that resembles enolization. The 4-methyl homolog behaves analogously. The hydroxy-anhydride is apparently the only isolable form[58] in the case of α,β-dimethyl-glutaconic acid.

Adipic and Pimelic Anhydrides.

Much of the material relating to the thermal decomposition of these anhydrides has already been given (p. 419) under the corresponding acids. Blanc's rule was mentioned in this connection. Cyclic ketones are formed as carbon dioxide is released from the molecule. Sometimes the change from acid to anhydride is a thermal one, but more frequently it is advantageous to employ acetic anhydride as a dehydrating agent. However, the change from anhydride to ketone (cyclopentanone, or cyclohexanone, etc.) is always a pyrolytic one. The reader is referred to the earlier chapter for the majority of these cases.

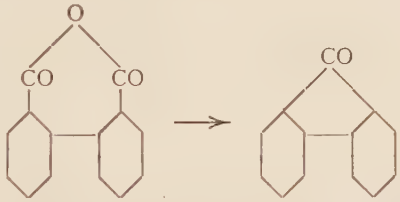
The effect of *gem.*[59] dimethyl groups[60] on this pyrolysis is illustrated

[55] Mol, *Rec. trav. chim.* **26**, 373 (1907).
[56] Leuchs and Manasse, *Ber.* **40**, 3243 (1907).
[57] Thole and Thorpe, *J. Chem. Soc.* **99**, 2236 (1911).
[58] Thole and Thorpe, *ibid.* p. 2216 and 2234.
[59] The prefix "*gem.*" is an abbreviation of gemini, meaning "twins"; therefore a *gem.* dimethyl group is $(CH_3)_2C=$ wherein two methyls are attached to a common carbon atom.
[60] Farmer and Kracovski, *J. Chem. Soc.* **1927**, 680.

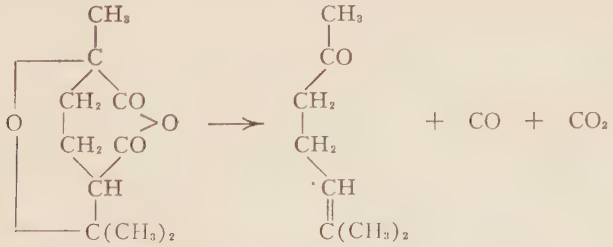
in the case of $\beta,\beta,\beta',\beta'$-tetramethyladipic anhydride, which becomes partially transformed into 1,1,2,2-tetramethyl-cyclopentane-4-one by long heating. $\alpha,\alpha,\alpha',\alpha'$-Tetramethyladipic anhydride fails to produce the corresponding cyclic ketone by slow distillation. At 1 mm. of pressure, adipic anhydride may also be distilled without change.

The anhydrides [61] of β,β-dimethyl- and β,β,ε-trimethyl-pimelic acids, by distillation at atmospheric pressure, are converted quantitatively into the corresponding cyclohexanones:

Fluorenone is in the cyclopentanone family; it may be synthesized in quantitative yields [62] from diphenic anhydride by maintaining it at the temperature of boiling sulfur:



Except for the instability of the cyclic ketone which would come by loss of carbon dioxide from cineolic anhydride,[63] the course of pyrolysis is undoubtedly the same as in the cases which have been mentioned. Methyl heptenone is the observed product of the dry distillation.



[61] Blanc, *Compt. rend.* **144**, 143 (1907).
[62] Graebe and Aubin, *Ann.* **247**, 265 (1888).
[63] Wallach and Gildemeister, *Ann.* **246**, 268 (1888); Wallach, *Ann.* **258**, 319 (1890); Wallach and Elkeles, *Ann.* **271**, 21 (1892).

CHAPTER 19.

AMIDES, ANILIDES, HYDRAZIDES, CYANIDES.

Amides, Anilides and Hydrazides.

Since amides are "ammono acids", it should be profitable to inquire whether or not their mechanism of decomposition simulates the corresponding "aquo acids". The formulas R—CH_2—CO—NH_2 and R—CH_2—CO—OH emphasize this similarity. Acids are quite stable to heat. The amides should be also. If the two fundamental equations (p. 334) for the pyrolysis of acetic acid lead to methane and to ketene, then an extension of these equations to acetamide would lead also to the prediction of methane and ketene:

Amide

$$CH_3—CO—NH_2 \rightleftharpoons \begin{cases} CH_4 + HN=C=O \\ NH_3 + CH_2=C=O \end{cases};$$

Acid

$$CH_3—CO—OH \rightleftharpoons \begin{cases} CH_4 + O=C=O \\ H_2O + CH_2=C=O \end{cases}$$

Following in the wake of these primary reactions, various secondary reactions are known to appear with acetic acid, and they would be anticipated with acetamide.

The pyrolysis of amides also presents a third possibility. In addition to the reactions of demethanation and of deammonation, there may also be the reaction of dehydration. As will be shown later, all three types have been realized in practice, but with simple amides, the dehydration into nitriles:

$$R—CO—NH_2 \longrightarrow R—C\equiv N + H_2O,$$

is especially prominent.

The behavior of the *S*-ethyl ester of thiocarbamic acid, smoothly decomposing[1] as it does in a tube at 150° into ethyl mercaptan and cyanuric acid, furnishes some confirmation of these speculations:

$$3C_2H_5S—CO—NH_2 \text{ (or } C_2H_5S—C(OH)=NH) \longrightarrow 3C_2H_5SH + (HNCO)_3.$$

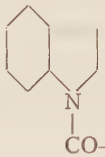
A further similarity of monoamides and of monocarboxylic acids in their pyrolytic behavior is the lack of any tendency for a direct change

[1] Pinner, *Ber.* **14**, 1083 (1881).

to a diacylated compound, $(RCO)_2NH$ or $(RCO)_2O$, by the elimination of ammonia or water, respectively. In the succinic or glutaric series, on the contrary, this is practically the exclusive reaction, succinic acid yielding its anhydride and succinamide changing into succinimide.

FORMAMIDE, H—CO—NH_2.

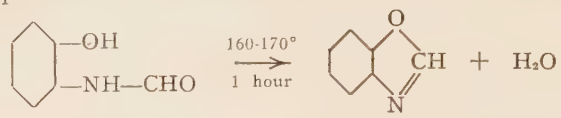
The use of Nernst's approximation formula leads to the prediction [2] of a complete dissociation of formamide into carbon monoxide and ammonia at 227° C. It also leads to the prediction [3] of a 70 percent conversion of formamide into water and hydrocyanic acid at 827° C. Both of these reactions proceed at 180-200°, the decomposition [4] into prussic acid (or ammonium cyanide) being noticeable when the temperature of the vapors exceeds 195°. Boehner and Andrews [5] observed only a 7.9 percent yield of hydrogen cyanide when formamide was slowly dropped on alumina which was maintained at 250-300°. Were formamide to pattern its pyrolysis after that of formic acid, one would expect not only ammonia and carbon monoxide, but also hydrogen and *iso*cyanic acid, H—N=C=O. These products seem not to have been observed or sought for.

The difference between formamide and acetamide may be inferred from the analogous examples of *N*-formyl indole,  , and *N*-acetyl indole. The former decomposes smoothly [6] in 6 hours at 300° into carbon monoxide and indole, whereas 2.6 grams of the latter gives but 40 cc. of carbon monoxide after 12 hours' heating at 300-350°. Part of the acetyl-indole is unchanged, part resinifies, and part changes into quinoline (0.2 gram). Formo-*o*-toluidide, $CH_3—C_6H_4—NH—CHO$, also changes [7] at 300° in a sealed tube to carbon monoxide and *o*-toluidine. These carbon monoxide eliminations reëmphasize the identity of the formyl radical and the aldehyde group.

In compounds, such as *o*-formylamino-phenol, which permit of ring closure by distillation, water is liberated [8] instead of carbon monoxide.

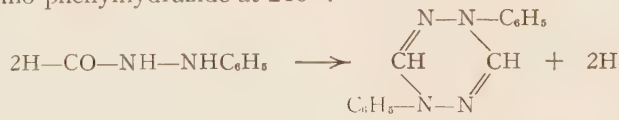
[2] Meyer and Orthner, *Ber.* **54**, 1705 (1921).
[3] Taylor, *Ind. Eng. Chem.* **18**, 959 (1926).
[4] Freer and Sherman, *Am. Chem. J.* **20**, 223 (1898).
[5] Boehner and Andrews, *J. Am. Chem. Soc.* **38**, 2503 (1916).
[6] Putochin, *Ber.* **59**, 1987 (1926).
[7] Ladenburg, *Ber.* **10**, 1129 (1877).
[8] Bamberger, *Ber.* **36**, 2051 (1903).

A yield of 2.5 grams of benzoxazole is obtained from 3 grams of the original compound.



o-formylamino-phenol *benzoxazole*

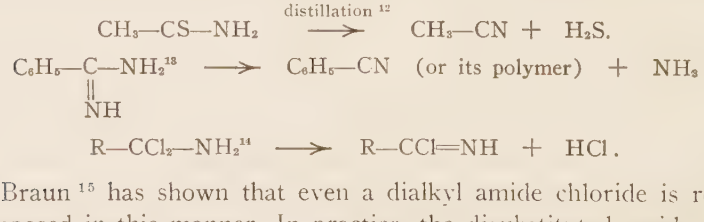
Diphenyl dihydrotetrazine [9] may be synthesized in slight yields by heating formo-phenylhydrazide at 210°:



Compounds Related to Acetamide.

The —C(=O)—H and —C(=O)—Cl groups display a tendency to eliminate carbon monoxide by heating, that is dormant in the —C(=O)—NH₂ or the —C(=O)—OCH₃ groups. The thermostability of the amide group may be appreciated when it is learned that less than 1 cc. of gas is produced at 300° from a 0.2 gram sample of triphenylacetamide,[10] $(C_6H_5)_3C—CONH_2$. Diphenyl-nitrogen, like triphenyl methyl, potentially is a free radical,[11] but tetraphenylurea, $(C_6H_5)_2N—CO—N(C_6H_5)_2$ is stable at least at 210°.

This stability is not shared, however by thioamides, amidines or amide chlorides. The latter in particular are very unstable. The general equations for their decompositions are:



Von Braun [15] has shown that even a dialkyl amide chloride is readily decomposed in this manner. In practice, the disubstituted amide reacts

[9] Bamberger, *Ber.* **30**, 1264 (1897).
[10] Bistrzycki and Landtwing, *Ber.* **41**, 686 (1908).
[11] Wieland and Schamberg, *Ber.* **53**, 1331 (1920).
[12] Henry, *Ann.* **152**, 148 (1869).
[13] Pinner and Klein, *Ber.* **11**, 6 (1878); Pinner, "Die Imidoaether und ihre Derivate," Berlin, Robert Oppenheim (Gustav Schmidt) **1892**, p. 154.
[14] Wallach, *Ann.* **184**, 4 (1877).
[15] von Braun and Weismantel, *Ber.* **55**, 3165 (1922).

with phosphorus pentachloride, and the resulting mixture is heated an hour at 110°:

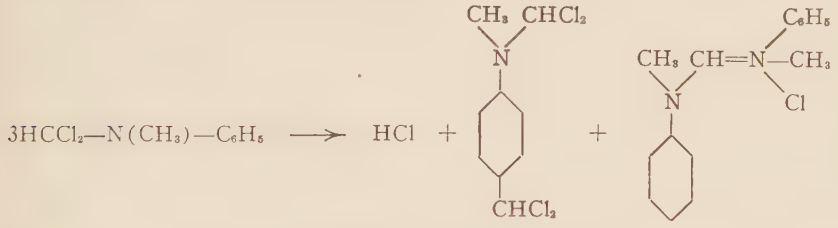
$$C_6H_5{-}CO{-}N\!<\!\begin{matrix}R'\\R''\end{matrix} \xrightarrow{PCl_5} \left[C_6H_5{-}CCl_2{-}N\!<\!\begin{matrix}R'\\R''\end{matrix}\right] \xrightarrow{heat} \begin{matrix}C_6H_5C{=}NR''\\|\\Cl\end{matrix} + R'{-}Cl.$$

If R′ represents the radical which is eliminated, then in compounds having the following radicals:

	R′	R″
1.	Benzyl	Methyl
2.	Methyl	Ethyl
3.	Ethyl	*n*-Propyl
4.	*n*-Propyl	*n*-Butyl

the ease of elimination is benzyl > methyl > ethyl > propyl > butyl.

The dichloro derivative of *N*-methyl-formanilide [16] behaves differently. By distilling it at 70° and 12 mm. it decomposes smoothly according to the following equation:



The compound, $Cl_2CH{-}C_6H_4{-}N(CH_3){-}CHCl_2$, is readily converted by alkali into *p*-methylaminobenzaldehyde, $H{-}CO{-}C_6H_5{-}NH{-}CH_3$, and this constitutes an effective method of synthesis. The yield is 20 grams from 60 grams of methyl formanilide.

These types of reaction mechanism all seem reasonable, yet it is noteworthy that in all cases the alkyl radical (R, in $RCSNH_2$, etc.) remains intact. There seems never to be an elimination of $HN{=}C{=}S$, $HN{=}C{=}NH$ (or $CN{-}NH_2$), or $HN{=}CCl_2$ corresponding to the elimination of $O{=}C{=}O$ from organic acids. Compounds with this type of formula (compare also $CH_2{=}C{=}O$) are evidently more to be expected from high temperature pyrolyses. These results make one wonder why it is that amides are so stable and show so little tendency to lose water with the formation of nitriles.

On p. 569 it has been pointed out that imide chlorides and bromides, $R{-}CX{=}NR'$ (R is aliphatic) may polymerize very readily to form the salt of a more complex base. This is not always the case, how-

[16] Vilsmeier and Haack, *Ber.* **60**, 119 (1927).

ever, since the imide chlorides $Cl_2CH—CCl=N—C_2H_5$ and especially $Cl_3C—CCl=N—C_2H_5$ can be distilled [17] without decomposition.

The spontaneous decomposition of formamidine-disulfide [18] into cyanamide illustrates the point that cyanamide may at times be eliminated from amidines:

$$H_2N—\underset{\underset{NH}{\|}}{C}—S—S—\underset{\underset{NH}{\|}}{C}—NH_2 \longrightarrow CN—NH_2 + S + HS—\underset{\underset{NH}{\|}}{C}—NH_2.$$

Acetamide and Its Homologs. It has been shown on p. 582 that acetamide may be expected to undergo three types of pyrolysis:

$$CH_3CONH_2 \longrightarrow CH_3—CN + H_2O$$
$$CH_3CONH_2 \longrightarrow CH_2=C=O + NH_3$$
$$CH_3CONH_2 \longrightarrow HNCO + CH_4$$

The first of these reactions was established by Boehner and Andrews,[5] who showed that 65-68 percent yields of acetonitrile could be realized by refluxing acetamide for four hours in contact with five parts by weight of alumina, pumice, glass, or graphite. Sand gives only a 52 percent yield. Provision was made for the distillation of the nitrile and water as fast as formed. Boehner [19] also found that this reaction of dehydration may be realized in 75-91 percent yields by passing the amide vapors (20 grams in 5 hours) in a current of air over these contact substances at 425°. The use of nitrogen instead of air is stated to lessen the yield. If acetamide vapors are passed through an *empty* tube in a current of air (at 425°), the yield of acetonitrile is but 10.8 percent as compared with 82 percent when alumina is the contact agent, and 91.5 percent when pumice stone is used. The order of efficiency for the contact materials in this process is: pumice stone, sand, alumina, graphite.

Recent experiments [20] at higher temperatures (680-720°) have confirmed this dehydration into acetonitrile as a major reaction, but have also identified appreciable quantities of methane and ketene, thereby demonstrating the existence of the other two concurrent reactions. Thus, if acetamide vapors are distilled through a quartz tube (packed with unglazed porcelain) at 500°, ketene may be identified in large amounts by passing the effluent gases into aniline. Yields of 43-45 percent ketene, based on the unrecovered acetamide, are realized. Since there is no reaction under these conditions between aniline and unused acetamide, the quantity of acetanilide produced is a direct measure of the quantity of ketene formed. No ketene is formed at temperatures as low as 375-

[17] von Braun, Jostes and Heymons, *Ber.* **60**, 92 (1927).
[18] Werner, *J. Chem. Soc.* **101**, 2167, 2178 (1912).
[19] Boehner and Ward, *J. Am. Chem. Soc.* **38**, 2505 (1916).
[20] Hurd and Martin, unpublished results.

425°; above 500°, the yields continue to be good and ketene may be identified even at 700°. The optimum temperature, however, is about 500°. In one run, 50 grams of original acetamide allowed recovery of 24 grams of it; from the other 26 grams was formed: water 4 grams; acetonitrile 10 grams; ammonium chloride (with HCl in the train) 2.6 grams; acetanilide (with aniline in the train) 27 grams. Another run, under duplicated conditions yielded 28 grams of acetanilide, and 22 grams of recovered acetamide. It must be kept in mind that the "recovered acetamide" may very well be "regenerated acetamide", at least to some extent, due to the reverse reaction:

$$NH_3 + CH_2{=}C{=}O \longrightarrow CH_3CONH_2.$$

The general reaction:

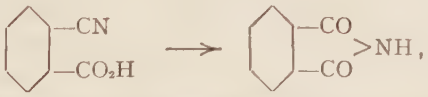
$$RCONH_2 \longrightarrow RCN + H_2O,$$

may be realized in 89-91 percent yields in the case of *propionamide*, *n-* and *iso-butyramide*, *isovaleramide* and *caproamide* by sweeping the amide vapors in a current of air over pumice stone at 425°. Sand gives equally high results and alumina gives slightly lower values. These results are those of Boehner and Ward,[19] and are strictly comparable to their results with acetamide.

Diacetamide[21] undergoes pyrolysis at 250° in a sealed tube (2 hours) into acetic acid and acetonitrile:

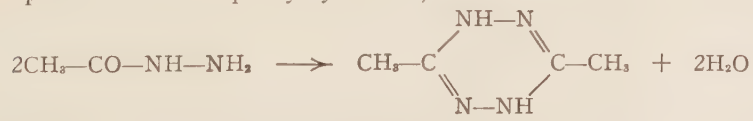
$$(CH_3CO)_2NH \longrightarrow CH_3CO_2H + CH_3CN.$$

Some acetamide also appears, formed by interaction of acetic acid and some of the unused diacetamide. Superficially, at least, this case and that of dibenzamide (p. 591) seem paradoxical if compared with the known behavior (p. 345) of *o*-cyanobenzoic acid:



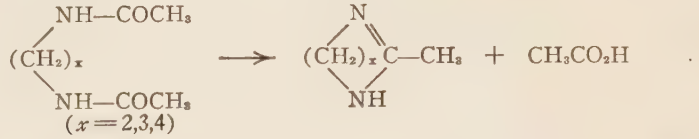
but the story at this point is incompletely told. It will be shown that at high temperatures phthalimide decomposes almost quantitatively into benzonitrile.

Acetohydrazide,[22] if heated at 180° for a long time, changes by dehydration into dimethyl dihydrotetrazine. Homologs behave similarly (see p. 584 for formo-phenylhydrazide).

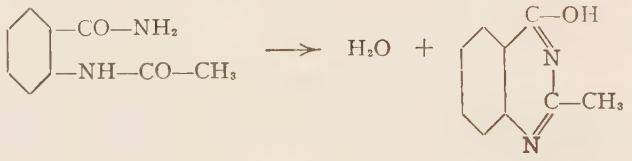


[21] Hentschel, *Ber.* **23**, 2396 (1890).
[22] Pellizzari, *Atti. accad. Lincei* [5] **8**, I, 330 (1899); Stollé, *J. prakt. Chem.* [2] **68**, 464 (1903).

The symmetrical diacetyl derivatives of the alkylene-diamines [23] undergo a ring closure to a certain extent when heated:

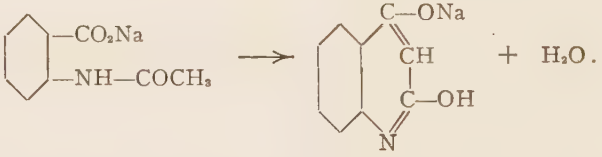


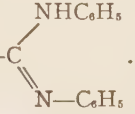
Ring closure of a somewhat similar nature results either by heating acetyl anthranilamide (*o*-carbamyl acetanilide) above its melting point [24] or by long heating with water:



Acetyl anthranilamide — *2-Methyl-4-hydroxy-quinazoline*

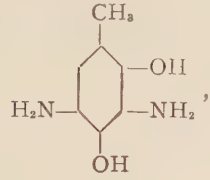
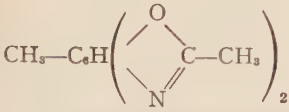
In much the same manner also, sodium acetylanthranilate changes almost quantitatively [25] at 150° into the sodium salt of γ-hydroxy-carbostyril:



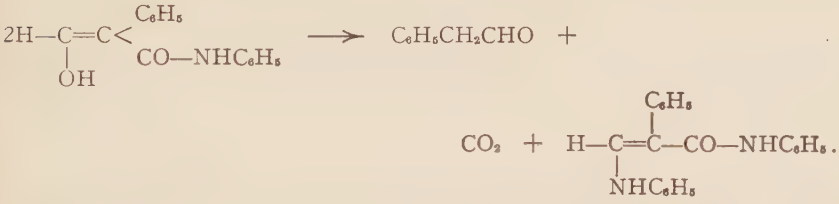
Acetanilide is stable [26] at moderately high temperatures, but more vigorous heating induces pyrolysis into a mixture of aniline, acetic acid, *o*-aminoacetophenone, and acetodiphenylamidine,  .

The sodium derivative of acetanilide, $C_6H_5N(Na)—COCH_3$, reacts with carbon dioxide to form a salt. At 130-140°, this undergoes [27] an interesting rearrangement into a derivative of malonic acid:

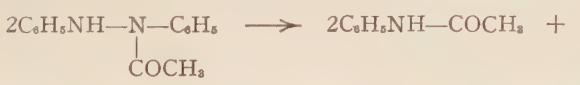
[23] Hofmann, *Ber.* **21**, 2332 (1888); Haga and Majima, *Ber.* **36**, 337 (1903).
[24] Weddige, *J. prakt. Chem.* [2] **36**, 143 (1887).
[25] D.R.P. 117,167; *Chem. Zentr.* **1901**, 1, 236.
[26] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[27] Seifert, *Ber.* **18**, 1358 (1885).

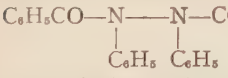
Dry distillation [28] of the tetraacetyl derivative of diaminocresorcinol,  , yields a rather complex substance,  , related to benzoxazole.

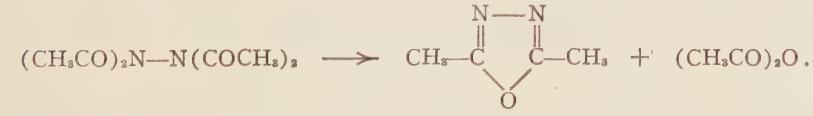
Formyl-phenyl-acetanilide [29] reacts with itself at 120-140° in an unusual reaction to produce phenyl-acetaldehyde:

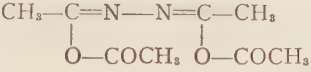


When acetyl hydrazobenzene is pyrolyzed,[30] the products of the reaction are acetanilide and azobenzene:



both of which are quite stable to heat. Dibenzoyl-hydrazobenzene,  , appears to decompose [31] similarly, yielding benzanilide and azobenzene, but tetraacetyl-hydrazine behaves far differently. When it is heated between 300-350°, it evolves acetic anhydride [32] and gives dimethyl-furodiazole:



Possibly this change is preceded by a migration of two of the acetyl groups from nitrogen to oxygen; thus,  .

[28] Henrich and Götz, *Ber.* **58**, 1055 (1925).
[29] Wislicenus and Erbe, *Ann.* **421**, 119 (1920).
[30] Stern, *Ber.* **17**, 379 (1884).
[31] Gilman and Pickens, *J. Am. Chem. Soc.* **47**, 2410 (1925).
[32] Stollé, *Ber.* **32**, 796 (1899).

Other Aliphatic Amides, Etc.

Either one or two mols of water may be expelled [33] from two mols of *lactamide,* depending on the temperature.

$$2CH_3{-}CHOH{-}CONH_2 \xrightarrow[\text{(sealed tube)}]{160^\circ} CH_3{-}CHOH{-}CO{-}NH{-}\underset{\displaystyle CONH_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}} + H_2O,$$

and

$$2CH_3{-}CHOH{-}CONH_2 \xrightarrow{170\text{-}220^\circ} C_6H_{10}N_2O_2 + 2H_2O.$$

The structure of "$C_6H_{10}N_2O_2$" is not known, except that it is stated to be not a diketopiperazine. Glycolamide follows the former reaction at 200° in a sealed tube:

$$2CH_2OH{-}CONH_2 \longrightarrow CH_2OH{-}CO{-}NH{-}CH_2{-}CONH_2 + H_2O.$$

Methyl-diglycolamide [34] changes into the cyclic ether-imide at 150°, by the loss of ammonia:

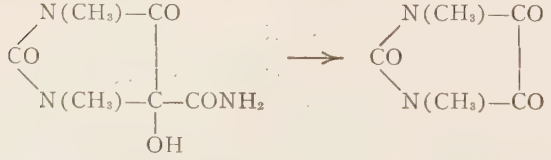
$$O\!<\!\begin{matrix}CH_2{-}CONH_2\\ CH_3{-}CH{-}CONH_2\end{matrix} \longrightarrow NH_3 + O\!<\!\begin{matrix}CH_2{-}CO\\ CH_3{-}CH{-}CO\end{matrix}\!>\!NH.$$

Although in this case there is a similarity in structure to lactamide, its behavior follows that of glutaramide (p. 583). A similar case, resembling succinamide in its behavior, although structurally related to glycollic acid, is that of thiocarbamid-glycollic acid [35] which decomposes in 30 minutes at 115°:

$$\begin{matrix}O{-}CS{-}NH_2\\ |\\ CH_2{-}CO{-}OH\end{matrix} \longrightarrow \begin{matrix}O{-}CS\\ |\\ CH_2{-}CO\end{matrix}\!>\!NH + H_2O.$$

With $-CONH_2$ instead of $-CSNH_2$, this reaction does not occur.

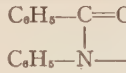
1,3-Dimethyl-5-hydroxy-hydantoyl-amide,[36] a more complex α-hydroxyamide, becomes degraded into cholesterophane when distilled:



Propiolamide,[37] and propiolanilide, $H{-}C{\equiv}C{-}CO{-}NHC_6H_5 . \frac{1}{2}H_2O$, change at their melting points (135° and 71° respectively) into acety-

[33] Schmuck, *Biochem. Z.* **147**, 193 (1924); *Chem. Abstracts* **19**, 470 (1925).
[34] Jungfleisch and Godchot, *Compt. rend.* **145**, 70 (1907).
[35] Ahlquist, *J. prakt. Chem.* **99**, 45 (1919).
[36] Biltz, *Ber.* **43**, 1589 (1910).
[37] Straus and Voss, *Ber.* **59**, 1689 (1926).

lene, carbon dioxide, and ammonia or aniline. Anhydrous propiolanilide decomposes also above its melting point, but whether or not acetylene and phenyl *iso*cyanate are the products of the pyrolysis is not known.

If heated in a distilling flask to 300°, cinnamyl-phenylhydrazide, $C_6H_5CH{=}CH{-}CO{-}NHNHC_6H_5$, undergoes a sudden vigorous reaction [38] yielding hydrogen and pyrazolone,  .

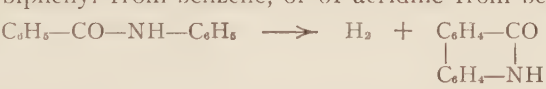
Aromatic Amides.

Nearly a century ago, Wöhler and Liebig [39] obtained small amounts of an oily liquid, later shown to be benzonitrile, by passing benzamide vapors through a red hot glass tube:

$$C_6H_5CONH_2 \longrightarrow C_6H_5CN + H_2O.$$

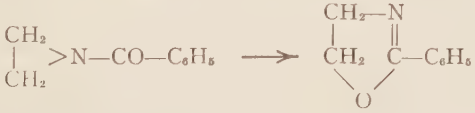
Boehner and Ward [19] showed that at 425°, a yield of 90.6 percent of the nitrile may be realized by passing benzamide vapors over alumina. Their work implies that sand or pumice stone could be used equally well in place of the alumina.

Excellent yields of phenanthridone [40] result from the pyrogenic decomposition of *benzanilide* vapors. This conversion is simply a dehydrogenation wherein the two aromatic nuclei participate. It resembles the synthesis of biphenyl from benzene, or of acridine from benzyl aniline.



Just as diacetamide (p. 587) was found to yield acetic acid and acetonitrile, so also *dibenzamide*, $(C_6H_5CO)_2NH$, changes into a mixture [41] of benzoic acid and benzonitrile by vacuum distillation. Di-*p*-toluylamide, $(CH_3C_6H_4{-}CO)_2NH$, even in a good vacuum becomes transformed [42] by distillation into *p*-toluic acid and *p*-tolunitrile. Di-*o*-toluylamide behaves similarly. Tribenzamide, $(C_6H_5CO)_3N$, sublimes without decomposition.

An interesting transformation of a 3-membered ring into a 5-membered ring occurs [43] during the distillation of benzoyl ethyleneimine. In this process, 2-phenyl oxazoline is formed:

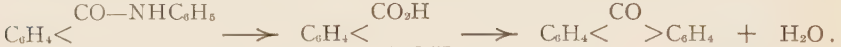


[38] Knorr *Ber.* **20**, 1107 (1887).
[39] Wöhler and Liebig, *Ann.* **3**, 249 (1832).
[40] Meyer and Hofmann, *Monatsh.* **37**, 681 (1916).
[41] Krafft, *Ber.* **23**, 2391 (1890).
[42] Krafft and Karstens, *Ber.* **25**, 454 (1892).
[43] Gabriel and others, *Ber.* **23**, 2493 (1890); **25**, 2383 (1892); **28**, 2933 (1895); **29**, 2381 (1896).

The hydrobromide of the oxazoline is produced when *N*-β-bromoethylbenzamide, $Br—CH_2—CH_2—NH—CO—C_6H_5$, is rapidly dissolved in hot water.

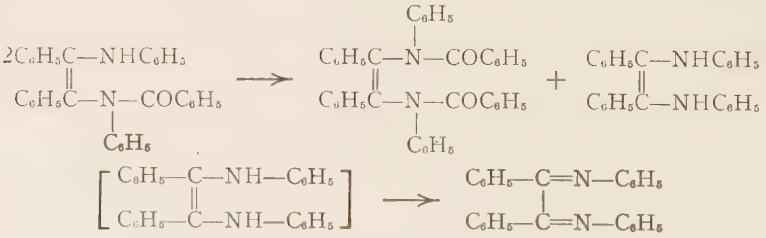
Thiobenzanilide, $C_6H_5—CS—NH—C_6H_5$, undergoes pyrolysis [43a] at 270-310° thereby producing 38-58 percent of 1-phenylbenzothiazole by loss of two atoms of hydrogen. It is considered that this hydrogen reduces some of the original anilide into aniline and thiobenzaldehyde, the latter of which changes into stilbene, tetraphenyl-thiophene and hydrogen sulfide. The aniline reacts with the original thiobenzanilide with the liberation of hydrogen sulfide, and the formation of 11-19 percent yields of symmetrical diphenylbenzenyl-amidine, $C_6H_5C(=NHC_6H_5)(NHC_6H_5)$. The yield of hydrogen sulfide is 37-40 percent.

The rather peculiar transformation from salicyl-anilide [44] to acridone by dry distillation from a retort heated on a sand bath is given the following mechanism:



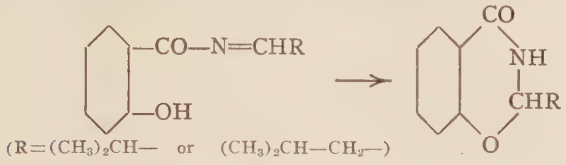
The pyrolysis occurs soon after the fusion, and at its conclusion there is a charred residue in the flask. In an identical fashion, salicyl-*o*-toluidide changes into 4-methyl acridone, and salicyl-*p*-toluidide into 2-methyl acridone. Traces of diphenylamine accompany the formation of acridone. It would seem that the reaction mechanism of Pictet and Hubert is not entirely satisfactory, for phenyl anthranilic acid, the intermediate product, is known [45] to pyrolyze almost exclusively into diphenylamine and carbon dioxide, with only traces of acridone.

The effect of heat (120-140°) on benzoyl-dianilinostilbene [46] is to induce a disproportionation into dibenzoyl-dianilinostilbene and dianilinostilbene, the latter, however, being unstable and decomposing further into benzil-dianil and benzanilide. The benzanilide is formed by atmospheric oxidation.



[43a] Chapman, *J. Chem. Soc.* **1928**, 1894.
[44] Pictet and Hubert, *Ber.* **29**, 1190 (1896).
[45] Graebe and Lagodzinski, *Ann.* **276**, 44 (1893).
[46] Everest and McCombie, *J. Chem. Soc.* **99**, 1761 (1911).

Fusion (150-160°) of *syn-iso*butylidine-salicylamide,[47] or *syn-iso*valeral-salicylamide, gives rise to metoxazones:



(R=$(CH_3)_2CH$— or $(CH_3)_2CH—CH_2$—)

Aromatic Hydrazides.

By heating benzohydrazide[48] at 180° dibenzoyl hydrazide is produced, and hydrazine or its decomposition products are evolved:

$$2C_6H_5CONHNH_2 \longrightarrow C_6H_5CONHNHCOC_6H_5 + N_2H_4.$$

Similarly, from 10 grams of salicyl hydrazide, 3.4 grams of disalicyl-hydrazide, $(HO—C_6H_4CONH—)_2$, is produced[49] following a 2 hour period at the boiling point of aniline, and another 2 hours at the boiling point of nitrobenzene. Two grams of the original material is recoverable, but a second reaction product, indazolone, $C_6H_4{<}^{CO}_{NH}{>}NH$, is isolable in 3.1 grams yield. This ring-closure, of course, depends on two reactive *ortho*-groups, but the other reaction type which is common to both benzohydrazide and salicylhydrazide, namely, the formation of a diacyl hydrazide from a monoacyl hydrazide, is a fundamentally different type of reaction from that encountered with monoacyl amides (p. 582).

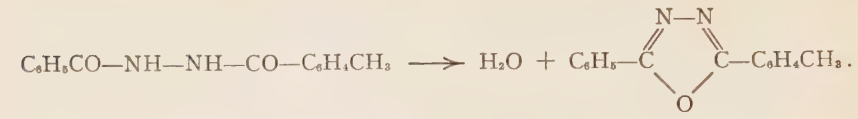
In many cases it is possible to synthesize hydrazides by heating the hydrazonium salt of the acid at 100° (p. 511). With the salt of *p*-bromo-benzoic acid,[50] however, the reaction does not stop there but instead gives the diacyl hydrazide. This transformation:

$$BrC_6H_4—CO_2N_2H_5 \longrightarrow \underset{\text{(not isolated)}}{[BrC_6H_4—CO—NHNH_2]} \longrightarrow (BrC_6H_4—CO—NH—)_2$$

comes with only a brief period of heating. The corresponding toluene salt, $CH_3C_6H_4—CO_2N_2H_5$, gives a mixture of the mono- and the di-acyl hydrazides.

The type of decomposition that may be expected from such diacyl hydrazides at higher temperatures[51] is illustrated with α-benzoyl-β-*p*-tolyl-hydrazide. In 30 minutes at 350° this compound loses a mol of water:

[47] Moucka and Rögl. *Ber.* **59**, 756 (1926).
[48] Curtius, *Ber.* **23**, 3029 (1890); *J. prakt. Chem.* [2] **52**, 219 (1895).
[49] Franzen and Eichler, *J. prakt. Chem.* [2] **78**, 162 (1908).
[50] Curtius and Franzen, *Ber.* **35**, 3241 (1902).
[51] Gilbert, *J. Am. Chem. Soc.* **49**, 286 (1927).



If the experiment is performed by suddenly subjecting 1 gram portions of the compound to a temperature of 450°, four-fifths of the rearrangement proceeds to aniline, carbon dioxide and benzonitrile, and one-fifth to *p*-toluidine. The reaction is completed in 5 minutes' time. Symmetrical dibenzoyl hydrazide behaves similarly, in which case aniline and phenyl cyanide are the products. Phenyl *iso*cyanate is regarded as an essential intermediate, and the mechanism is undoubtedly very similar to the Lossen rearrangement of hydroxamic acids (see p. 674). The steps are as follows:

$$Ar—CO—NH—NH—CO—Ar \longrightarrow Ar—C{\equiv}N + H_2O + [{=}N—CO—Ar]$$

$$[{=}N—CO—Ar] \longrightarrow Ar—N{=}C{=}O,$$

whence,

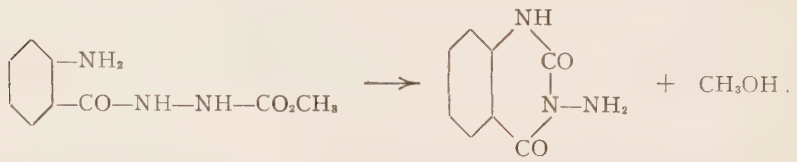
$$Ar—NCO + H_2O \longrightarrow ArNH_2 + CO_2.$$

With α-benzoyl-β-*p*-chlorobenzoyl hydrazide, three times more *p*-chloroaniline is formed than aniline, but otherwise the results are strictly comparable. Such results as these may be of value in a study of relative electron attractions of radicals (p. 26).

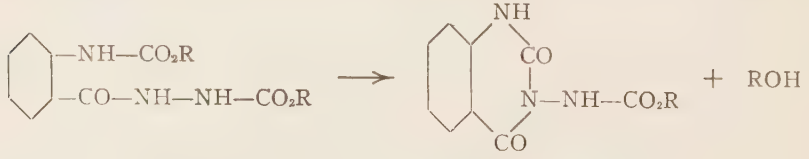
Ammonia is evolved from *p*-aminobenzohydrazide [52] between 220-280°; *p*-benzoisopyrazolone is formed:

$$H_2N—C_6H_4—CONHNH_2 \longrightarrow NH_3 + (C_7H_6ON_2)_x.$$

o-Aminobenzocarbomethoxy-hydrazide [53] may be transformed into a 70 percent yield of 3-amino-2,4-diketotetrahydro-quinazoline (3-amino-benzoylene urea) by heating it for 2 hours at 180-200°:

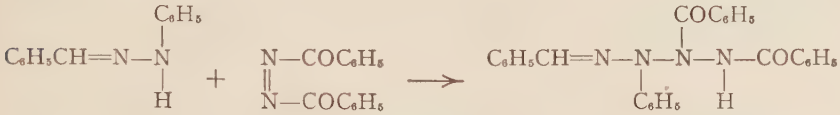


The pyrolysis of *o*-carbomethoxaminobenzcarbomethoxy-hydrazide at 180° into 3-carbomethoxamino-benzoylene urea (70 percent yield) is similar:

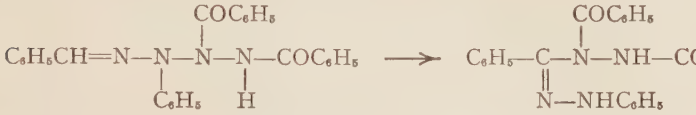


[52] Heller and Gottfried, *J. prakt. Chem.* 111, 368 (1925).
[53] Heller and Siller, *ibid.* 116, 1 (1927).

Phenyl-benzal-dibenzoyl-tetrazane [54] is synthesized by the following reaction:

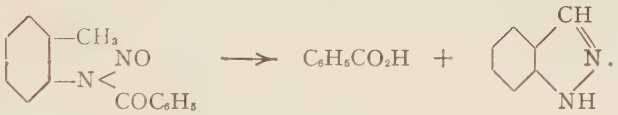


A few degrees above its melting point, 139°, this tetrazane rearranges to the monophenylhydrazone of tribenzoyl-hydrazide:



When the *p*-bromophenylhydrazone of benzaldehyde is substituted for benzaldehyde-phenylhydrazone in the above series of reactions, the tetrazane cannot be isolated, but instead the reaction proceeds directly to the product of rearrangement.

One of the best synthetic methods for indazole consists in the thermal decomposition [55] of *N*-nitroso-benzo-*o*-toluidide, especially in warm benzene:



Amides and Hydrazides of Dibasic Acids.

If oxamide [56] is heated until it has sublimed completely, there is formed in the condensed vapors 2.9 percent of ammonium cyanate and 4.18 percent of urea. Ammonia, carbon monoxide and hydrocyanic acid are also evolved in this process. Only a small amount of dimethyl oxamide suffers decomposition by sublimation but the course of the reaction seems to be in accord with the ensuing equation:

A mixed amide and hydrazide might be expected to form a diacylated hydrazide since this is a property of hydrazides, and since amides as such are quite stable. This is precisely what occurs with semioxamazide. This substance [57] melts at 220° with the same type of decomposition that may be induced by two hours' heating in a

[54] Busch, Muller and Schwarz, *Ber.* **56**, 1600 (1923).
[55] Jacobson and Huber, *Ber.* **41**, 660 (1908).
[56] Werner and Carpenter, *J. Chem. Soc.* **113**, 699 (1918).
[57] Kerp and Unger, *Ber.* **30**, 585 (1897).

sealed tube at 145°. Cyclo-oxalylhydrazide, $\begin{matrix}CO{-}NH\\ |\quad\ |\\ CO{-}NH\end{matrix}$, and its dimer, $\begin{matrix}CO{-}NH{-}NH{-}CO\\ |\qquad\qquad |\\ CO{-}NH{-}NH{-}CO\end{matrix}$, are produced as ammonia is evolved:

$$H_2N{-}CO{-}CO{-}NH{-}NH_2 \longrightarrow NH_3 + \begin{matrix}CO{-}NH\\ |\quad\ |\\ CO{-}NH\end{matrix}.$$

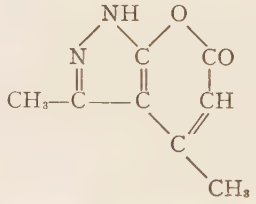
Ammonium cyanate and urea are also present.

Wilson and Pickering[58] have extended our knowledge of this type of pyrolysis to the ketone-semioxamazones, $H_2N{-}CO{-}CO{-}NH{-}N{=}CR_2$. With R groups such as methyl, ethyl, phenyl or benzyl, the pyrolysis is complete in 2-4 hours at about 220°. If one of the groups is $-CH_2CO_2C_2H_5$, the decomposition proceeds at 130°. In general the results are well explained by assuming an initial disproportionation:

$$\begin{matrix}CONH_2\\ |\\ CONH{-}N{=}CR_2\end{matrix} \longrightarrow \begin{matrix}CONH_2\\ |\\ CONH_2\end{matrix} + \begin{matrix}CO{-}NH{-}N{=}CR_2\\ |\\ CO{-}NH{-}N{=}CR_2\end{matrix}$$

ketone-semioxamazone — *oxamide* — *oxalyl-dihydrazones*

The intermediate oxalyl-dihydrazones are usually not isolated except in small amounts, but they decompose further into *cyclo*oxalyl hydrazide, $\begin{matrix}CO{-}NH\\ |\quad\ |\\ CO{-}NH\end{matrix}$, and ketazines, $R_2C{=}N{-}N{=}CR_2$. These ketazines are usually stable at these temperatures, but when $=CR_2$ represents $=C<\begin{matrix}CH_3\\ CH_2CO_2Et\end{matrix}$ there is a further decomposition[59] into 3,4-dimethyl-1,2-pyrazo-6,7-pyrone,



. This occurs by the loss of two molecules of alcohol. The same pyrone derivative, together with hydrazine and 4-aminourazole as reaction products, may be prepared by maintaining ethyl acetoacetate δ-aminosemicarbazone,[59a] $\begin{matrix}CH_3{-}C{-}CH_2{-}CO_2Et\\ \|\\ N{-}NH{-}CO{-}NHNH_2\end{matrix}$, at its melting point. If instead, the heating is performed in boiling alcohol, there is merely disproportionation

[58] Wilson and Pickering, *J. Chem. Soc.* **127**, 965 (1925).
[59] *Cf.* Bülow and Lobeck, *Ber.* **40**, 708 (1907); Bülow and Schaub, *Ber.* **41**, 1945 (1908); Wolff and Schreiner, *Ber.* **41**, 550 (1908).
[59a] Munro and Wilson, *J. Chem. Soc.* **1928**, 1257.

into hydrazine and di(ethyl acetoacetate)-hydrazidicarbohydrazone, $(CO(NH{-}N{=}CMe{-}CH_2CO_2Et){-}NH{-})_2$. Dibenzaldehydehydrazidicarbohydrazone breaks down in 3 hours at 250° with the production of benzylidene azine and 4-aminourazole. The following reaction [59b] occurs on boiling in absolute alcohol:

$$CO(NH{-}N{=}CHPh)_2 \longrightarrow \underset{\textit{dibenzaldehyde-hydrazidicarbohydrazone}}{(-NH{-}CO{-}NH{-}N{=}CHPh)_2} + \underset{\textit{benzylidene azine}}{(PhCH{=}N{-})_2}$$

Malonamide is a fairly stable structure, which seems not to have been studied for its pyrolytic behavior. Diaminomalonamide, $(H_2N)_2C(CONH_2)_2$, loses a molecule of ammonia [60] at 90-100°, but not by interaction of the amide groups. The compound formed has the structure $HN{=}C(CONH_2)_2$.

Also, in the malonamic acids, it is the carboxyl and not the carbamido group which suffers by heating. Thus, β-ethyl-δ-phenyl allylmalonamic acid, $C_6H_5CH{=}CH{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}{-}CH{<}\begin{matrix}CO_2H\\CONH_2\end{matrix}$, loses carbon dioxide at its melting point [61] (165°) and yields β-ethyl-δ-phenyl allylacetamide. Compounds with the half-nitrile structure, $\underset{\displaystyle CN}{\underset{|}{R{-}CH}}{-}CO_2H$, behave similarly. See pages 336 and 339.

Succinamide and related compounds undergo pyrolysis quite generally into the imide. Succinamide melts at 242°; at higher temperatures this decomposition [62] sets in:

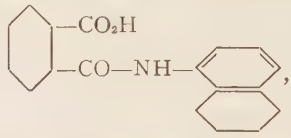
$$\begin{matrix}CH_2{-}CONH_2\\|\\CH_2{-}CONH_2\end{matrix} \longrightarrow \begin{matrix}CH_2{-}CO\\|\\CH_2{-}CO\end{matrix}{>}NH + NH_3.$$

Succinamic acid, $HO_2C{-}CH_2CH_2CONH_2$, undergoes this change into the imide at a somewhat lower temperature (200°). Observe that there is no tendency for the alternative formation of succinic anhydride. Ethyl succinic anil, $\begin{matrix}C_2H_5{-}CH{-}CO\\|\\CH_2{-}CO\end{matrix}{>}N{-}C_6H_5$, results from ethyl succinic acid anilide [63] by heating for 90 minutes at 180°.

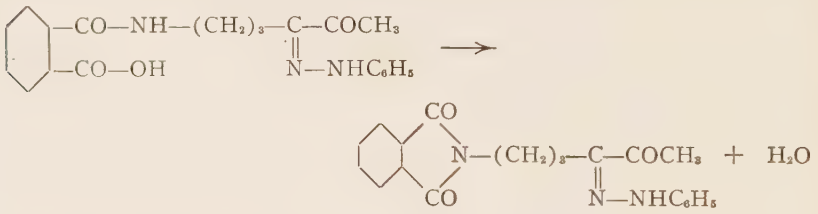
Phthalamide, and phthalamic acid change so easily into phthalimide that they are fairly uncommon compounds. Similarly, pyromellitic tetramide changes [64] on heating into pyromellitic imide,

[59b] Wilson, Baird, Brown and Pickering, *J. Roy. Tech. Coll. Glasgow,* No. 4, 60 (1927), *Chem. Abstracts* 22, 3394 (1928).
[60] Conrad and Brückner, *Ber.* 24, 3003 (1891).
[61] MacLeod, *Am. Chem. J.* 44, 349 (1910).
[62] Serda and Wiedemann, *Ber.* 23, 3286 (1890).
[63] Carrière, *Ann. chim.* 17, 38 (1921).
[64] Meyer and Steiner, *Monatsh.* 35, 391 (1914).

$C_6H_2((CO)_2NH)_2$. There are a few recent investigations dealing with the pyrolysis of *N*-substituted phthalamic acids; such, for example, as

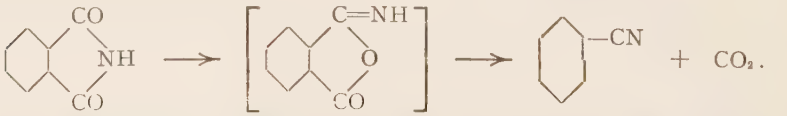
α-tetralyl-phthalamic acid,  , which melts with

decomposition [65] at 182° giving the imide. The *β*-isomer behaves analogously at 157°. The ring closure in the following case, namely, the change at 180° *in vacuo* from *ζ*-*o*-carboxy-benzaminohexane-*β*,*γ*-dione-*γ*-phenylhydrazone [66] into *ζ*-phthaliminohexane-*β*,*γ*-dione-*γ*-phenylhydrazone, is one of strictly analogous type:



In this case, the yield is only 10-20 percent, but since the reaction is a dehydration it does not occasion surprise to learn of a 70 percent yield when the substance is heated with acetic anhydride.

Phthalimide [67] is a reasonably stable substance, but at 350° it starts to decompose, and at 480° it is almost quantitatively converted into benzonitrile. Possibly this takes place through *iso*phthalimide:



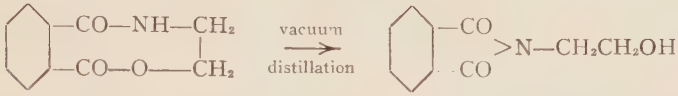
Benzonitrile is an extremely stable compound towards heat. It remains unaltered unless the temperature is high enough for complete breakdown. 4-Chlorophthalimide is more stable than phthalimide. Even at 500° the pyrolysis to *p*-chlorobenzonitrile proceeds slowly. Tetrachlorophthalimide, $C_6Cl_4{<}^{CO}_{CO}{>}NH$, gives only enough nitrile at 600° to be tested by its odor.

It has been apparent that these cases, related to succinamide and phthalamide, have undergone pyrolysis into the imide rather than to the anhydride. Camphoramic acid, however, appears to behave differ-

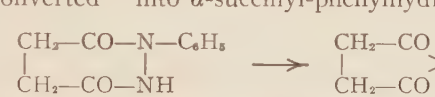
[65] Schroeter and others, *Ann.* **426**, 17 (1922).
[66] Manske, Perkin, Jr., and Robinson, *J. Chem. Soc.* **1927**, 1.
[67] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).

ently in spite of the statement of Laurent [68] that water and camphoric imide were produced. Claisen and Manasse [69] report that by heating camphoramic acid, $C_8H_{14}<^{CONH_2}_{CO_2H}$, above its melting point, camphoric anhydride, $C_8H_{14}<^{CO}_{CO}>O$, and ammonia are formed. (See p. 517, above.)

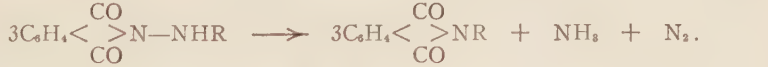
Another case, of a somewhat different type, again furnishes evidence for the preferential pyrolysis to the imide:[70]



By distillation of *β*-succin-phenylhydrazide at ordinary pressure, it becomes converted [71] into *α*-succinyl-phenylhydrazide:



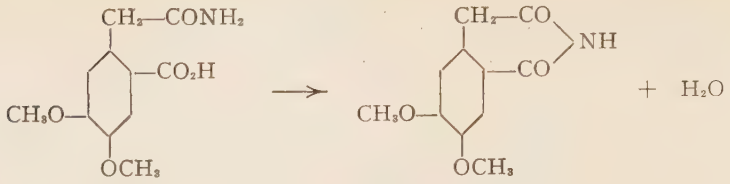
As would be expected, the *phthalyl hydrazides* are much less stable than phthalimide or than the phthalanils. At a definite temperature, the former undergo a vigorous exothermic reaction [72] in which ammonia and nitrogen are evolved, and a phthalanil is formed:



For phthalyl-phenylhydrazide, the temperature of decomposition is 346°; a trace of phthalimide may be detected in the reaction product. With the *p*-bromophenylhydrazide, the pyrolysis is similar except that hydrogen bromide is also evolved in considerable amounts. The *o*- or the *p*-tolylhydrazides undergo pyrolysis into the anils at about 360°.

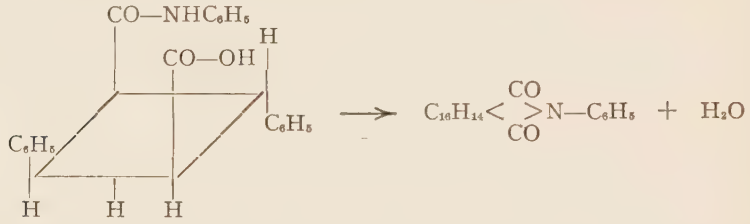
Glutarimide may be formed from the amide by heat; ammonia is liberated at the melting point [73] (176°), thus resembling the formation of succinimide. In more complex amides which contain the glutaric functional group, the same situation exists. Thus, 4,5-dimethoxy-homophthalamic acid melts with decomposition [74] to the imide at 204°. The imide may also be formed, as is usually the case, by heating the ammonium salt.

[68] Laurent, *Ann.* **60**, 326 (1846).
[69] Claisen and Manasse, *Ann.* **274**, 80 (1893).
[70] Gabriel, *Ber.* **38**, 2397, 2407 (1905); **45**. 1648 (1912).
[71] Michaelis and Hermens, *Ber.* **25**, 2747 (1892); **26**, 674 (1893); Ponzio and Valente, *Gazz. chim. ital.* **38**, I, 520 (1908).
[72] Chattaway, Cumming and Wilsdon, *J. Chem. Soc.* **99**, 1950 (1911).
[73] Pinner, *Ber.* **23**, 2943 (1890).
[74] Haworth and Pink, *J. Chem. Soc.* **127**, 1368 (1925).



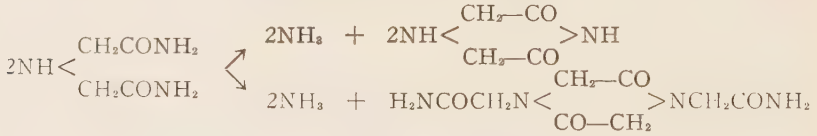
Similarly, 4,5-methylenedioxy-homophthalamic acid changes into the imide by fusion.

γ-Truxillanilidic acid becomes dehydrated in the usual manner at 240°, yielding γ-truxillphenylimide. This case also possesses the functional group of the glutaric series.

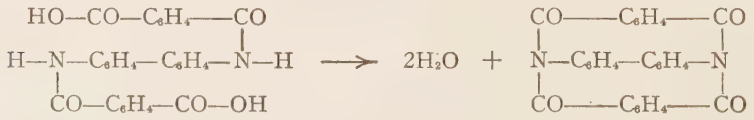


Similarly, γ-truxillamidic acid is found [75] to change into the imide by fusion (melting point 240°). Somewhat better results are obtained by heating the ammonium salt of γ-truxillic acid.

Another substance which may be considered here, because of a 3-atom chain separating the two amido groups, is the diamide of diglycolamic acid. If pyrolyzed [76] at 15 mm. 2,6-diketopiperazine is produced. There is a concurrent reaction, however, as indicated by the equations:

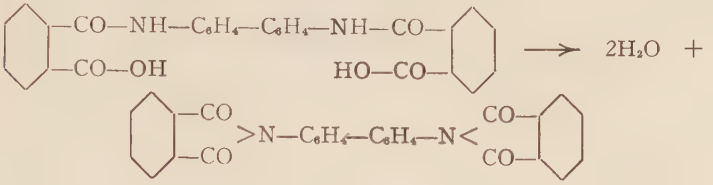


Diphenyl-4,4′-diphthalamic acid is completely converted into diphthalylbenzidine at 130-140°, by heating [77] for 2 hours in a hydrogen atmosphere. Shimomura advances the following mechanism:



[75] Stoermer, Wegner and Carl, *Ber.* **56**, 1683 (1923); Stoermer and Fretwurst, *Ber.* **58**, 2718 (1925).
[76] Jongkees, *Rec. trav. chim.* **27**, 305 (1908).
[77] Shimomura, *Mem. Coll. Sci. Kyoto Imp. Univ. A* **8**, 19 (1925); *Chem. Abstracts* **19**, 2196 (1925).

Since this reaction may be reversed by the use of alkali, the evidence for the more customary type of "phthalimide ring closure" seems equally good, if not preferable. The equation would then be:



Cyanides.

Inorganic Cyanides.

When strongly heated either in an atmosphere of helium or of nitrogen, sodium cyanide [78] decomposes into sodium acetylide, sodium, carbon and nitrogen. The partial pressures of these components, at 1050° (helium), in mm. of mercury are: Sodium, 117 mm.; nitrogen, 108 mm.; sodium carbide, 21 mm.; sodium cyanide, 21 mm.

Mercuric cyanide [79] is easily decomposed (400°) into mercury and cyanogen. At a bright red heat, potassium ferrocyanide yields potassium cyanide, iron carbide and nitrogen:

$$K_4Fe(CN)_6 \longrightarrow 4KCN + FeC_2 + N_2.$$

It is more economical to convert potassium ferrocyanide into a mixture of potassium cyanide and sodium cyanide by heating in the presence of metallic sodium:

$$K_4Fe(CN)_6 + 2Na \longrightarrow 4KCN + 2NaCN + Fe.$$

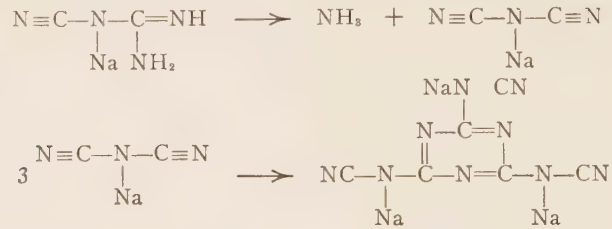
Potassium- or thallium-ferricyanides ($Tl_3Fe(CN)_6$) decompose [80] somewhat similarly by prolonged heating, except that cyanogen is liberated:

$$2K_3Fe(CN)_6 \longrightarrow 6KCN + 2FeC_2 + 2N_2 + (CN)_2.$$

This pyrolysis starts very slowly at 230° insofar as weight changes are concerned, although the color changes from red to green at 160°. When hydrogen ferrocyanide, $H_4Fe(CN)_6$, is heated [81] at 300° in the absence of air, it yields a pale yellow powder which is probably a ferrous ferrocyanide, $Fe_2(Fe(CN)_6)$. Ferrous cyanide pyrolyzes into iron carbide, iron nitride, iron, carbon and nitrogen.

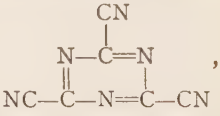
[78] Guernsey and Sherman, *J. Am. Chem. Soc.* **48**, 695 (1926).
[79] Perry and Bardwell, *J. Am. Chem. Soc.* **47**, 2629 (1925).
[80] Cuttica, *Gazz. chim. ital.* **52**, I, 20 (1922).
[81] Browning, *J. Chem. Soc.* **77**, 1234 (1900); Mittasch, Kuss and Emert, *Z. anorg. allgem. Chem.* **170**, 193 (1928).

If sodium dicyanamide, $NaN(CN)_2$, is heated [82] to dull redness over a free flame, it is changed into sodium tricyanomelamine, a polymer, with the liberation of little or no gas. This substance is also formed by heating sodium dicyandiamide, but in this case, ammonia is evolved and sodium dicyanamide is an intermediate product:



The existence of a subcarbide of calcium,[83] such as CaC, was postulated by Ehrlich as a pyrogenic product from calcium cyanamide, CaNCN, above 1000°. This, however, has been denied [84] by Ruff and Foerster, who found that pure calcium carbide (CaC_2) melts near 2300°. Kameyama [85] also entered a denial and reported no evidence of pyrolysis at temperatures below 1140°; above 1250°, calcium cyanamide sublimes readily.

Organic Cyanides.

Cyanogen, itself, decomposes into its elements at high temperatures. This may occur [86] in part at 200° and 300 atmospheres. If cyanogen is maintained for a long time at 400° (at one atmosphere) it polymerizes to paracyanogen, $(CN)_x$. Hexacyanogen,[87]  , boils at 262° without decomposition, but it changes quantitatively into cyanogen when it is passed over a red hot platinum spiral.

The compounds, C=N—C≡N and C=N—N=C, which would be of great theoretical interest, have never been isolated.

Between 200-300°, cyanuric iodide decomposes [88] into paracyanogen and iodine. Two molecules of cyanamide [89] combine at 150° with the formation of dicyandiamide:

[82] Madelung and Kern, *Ann.* **427**, 26 (1922).
[83] Ehrlich, *Z. Elektrochem.* **28**, 529 (1922).
[84] Ruff and Foerster, *Z. anorg. allgem. Chem.* **31**, 321 (1923).
[85] Kameyama, *J. Faculty Eng., Tokyo Imp. Univ.* **13**, 73 (1923); *Chem. Abstracts* **18**, 3155 (1924).
[86] Buff and Hofmann, *Ann.* **113**, 136 (1860); Berthelot, *Compt. rend.* **95**, 955 (1882); Schutzenberger and Schutzenberger, *ibid.* **111**, 774 (1890); Briner and Wroczynski, *Compt. rend.* **151**, 314 (1910).
[87] Ott, *Ber.* **52**, 663 (1919).
[88] Klason, *J. prakt. Chem.* [2] **34**, 157 (1886).
[89] Beilstein and Geuther, *Ann.* **123**, 241 (1862); Drechsel, *J. prakt. Chem.* [2] **11**, 301 (1875); **13**, 331 (1876).

$$2CN{-}NH_2 \longrightarrow CN{-}NH{-}\underset{\displaystyle NH_2}{\underset{|}{C}}{=}NH$$

A third molecule enters combination with more vigorous heating to produce melamine, $H_2N{-}\underset{\displaystyle N{-}\underset{\displaystyle NH_2}{\underset{|}{C}}{=}N}{\underset{\|}{C}}{-}N{=}\underset{|}{C}{-}NH_2$, together with some melam and ammonia. Above 100°, cyanamide hydrochloride, $H_2CN_2.2HCl$, yields hydrogen chloride and mellon.[90] If the ammonium salt of carbethoxycyanamide, $NC{-}N(NH_4){-}CO{-}OC_2H_5$, is maintained for two hours at 105-110°, there is an initial fusion which is followed by gradual solidification to impure amelide ($C_3H_4O_2N_4$) as ammonia is liberated.

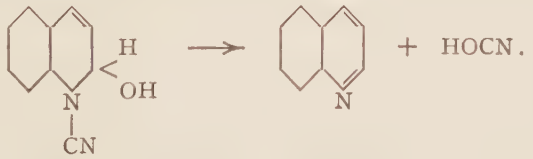
The great stability of phenyl cyanide has already been mentioned (p. 598) in connection with its formation during the pyrogenic decomposition of phthalimide. Pure benzonitrile,[91] or pure *p*-toluonitrile, exhibits absolutely no tendency to polymerize even after years of storage at room temperature. 2-Hydroxy-5-nitro-benzonitrile polymerizes [92] to the trimer, however, if it is held above its melting point, 190°. The same is true of 3,5-dibromosalicylonitrile. Whether or not benzonitrile would gradually polymerize if maintained at about 200° cannot be stated.

In some cases, the rearrangements of *iso*cyanides into nitriles by heat have been fairly well established. Thus,[93] on heating three hours between 230-255° ethyl *iso*cyanide is converted into propionitrile, but there is some polymerization as well. By heating phenyl *iso*cyanide,[94] benzonitrile is formed:

$$C_6H_5NC \longrightarrow C_6H_5CN,$$

According to Weith the conditions of reaction were a temperature of 200-220° for 2-3 hours in a sealed tube.

A rather unusual compound, dihydrohydroxy-cyano-quinoline,[95] evolves cyanic acid when it is heated:



[90] Pinck and Hetherington, *Ind. Eng. Chem.* **18**, 629 (1926).
[91] Johnson and Bass, *J. Am. Chem. Soc.* **44**, 1342 (1922).
[92] Lindemann and Thiele, *Ann.* **449**, 72 (1926).
[93] Nef, *Ann.* **280**, 296 (1894).
[94] Weith, *Ber.* **6**, 213 (1873).
[95] von Braun, *Chem. Zentr.* **1909**, II, 1902; *Chem. Abstracts* **5**, 888 (1911).

CHAPTER 20.

UREA, ISOCYANATES, AND RELATED COMPOUNDS.

The century-old synthesis of urea by Wöhler is usually regarded as a turning point in the history of organic chemistry. This change from ammonium cyanate into urea is, therefore, a rearrangement possessing unusual interest. Investigations in the past decade by E. A. Werner have shown that the synthesis of urea by this method and by all other methods have one point in common, namely, that ammonia must ultimately react with *iso*cyanic acid. According to Werner, the customary formula for urea does not adequately represent the facts, either for the synthesis or for the reactions of urea. Instead of carbamide, $H_2N—CO—NH_2$, he advocates for the urea formula either $HN{=}C{<}^{O}_{NH_2}$ or $NH{=}C{<}^{OH}_{NH_2}$. The equation for any synthesis of urea, therefore, is:

$$H—N{=}C{=}O \;+\; H—NH_2 \longrightarrow HN{=}C{<}^{OH}_{NH_2}.$$

Parenthetically, it may be noted that substituent groups, such as phenyl in diphenylurea, are considered to modify this structure to such an extent that a formula of the carbamide type results.

For an intelligent appreciation of the reactions of urea, therefore, a discussion of the interrelation of cyanic and *iso*cyanic acids must be included. A mixture of these substances may be prepared by dry-distilling cyanuric acid and condensing the gas in a freezing mixture:

$$(HNCO)_3 \longrightarrow 3HNCO, \text{ or } 3HOCN.$$

The relative amount of the keto and the enol forms of cyanic acid in this distillate, as revealed by polymerization experiments at various temperatures to cyanuric acid and cyamelide respectively, is shown to favor the enol form, H—O—C≡N, at low temperatures. With increasing temperatures, there appear increasing amounts [1] of the keto isomer, O=C=N—H. Thus, it is estimated that at 0° there is an equilibrium mixture of 60 percent of the enol and 40 percent of the keto form,

[1] Werner and Fearon, *J. Chem. Soc.* 117, 1356 (1920).

whereas at 20° it is 43 percent of the enol and 57 percent of the keto form.

This information concerns the reactions to follow since ammonia unites with the enol form to produce ammonium cyanate, and with the keto form to give urea. The keto form, being an *iso*cyanate, may also unite with urea to give biuret. These products are usually among the compounds present when urea, or a related substance, is pyrolyzed.

The pyrogenic decomposition [2] of triethyl cyanurate, by slowly passing the vapors in a high vacuum over a platinum spiral heated to a pale red, gives cyanic acid and ethylene. The pyrolysis follows the normal mode of decomposition for ethyl esters, with the added feature that the cyanuric acid which would be momentarily formed becomes depolymerized, as it is wont to do at high temperatures.

Carbamide is one of the few substances containing the $=C(NH_2)_2$ group. Diamino-malonamide is another such substance, and it breaks down [3] at 90-100° with the evolution of ammonia:

$$(H_2N)_2C(CONH_2)_2 \longrightarrow NH_3 + HN{=}C(CONH_2)_2.$$

Thermal Methods for the Synthesis of Urea.

From the foregoing, it will be apparent that Wöhler's synthesis [4] of urea may be analyzed into the following steps:

Dissociation

$$NH_4{-}O{-}CN \longrightarrow NH_3 + HOCN$$

Rearrangement

$$HOCN \rightleftharpoons HNCO$$

Combination

$$HNCO + NH_3 \longrightarrow HN{=}C(OH){-}NH_2$$

The formation of urea, and of substituted ureas, by heating ammonium carbamates [5] is particularly instructive in connection with the problem of the structure of urea. This has already been set forth in the chapter on ammonium salts (p. 513). Very definitely, this reaction cannot consist of the simple dehydration of an ammonium salt into an amide.

In the preparation of urea from carbonyl chloride, the very low yield [6] which is produced (only 4.6 percent of urea is formed if the phosgene is in excess, and but 30-40 percent if the ammonia is in excess) is explained by Werner in the following steps:

[2] Kesting, *J. prakt. Chem.* **105**, 242 (1923).
[3] Conrad and Brückner, *Ber.* **24**, 3003 (1891).
[4] Wöhler, *Pogg. Ann.* **15**, 622 (1829); *Ann. chim. phys.* [2] **43**, 67 (1830).
[5] Werner, *J. Chem. Soc.* **117**, 1046 (1920).
[6] Werner, *J. Chem. Soc.* **113**, 694 (1918).

$$\underset{\text{carbonyl chloride}}{COCl_2} \xrightarrow{NH_3} \underset{\text{carbamyl chloride}}{NH_2{-}COCl} \longrightarrow HCl + \underset{\text{isocyanic acid}}{HNCO} \longrightarrow \underset{\text{cyanuric acid}}{(HNCO)_3}$$

$$\underset{\text{isocyanic acid}}{HNCO} \xrightarrow{NH_3} \underset{\text{urea}}{HN{=}C(OH)NH_2} \xrightarrow[HNCO]{NH_2COCl\ or} \text{biuret} \xrightarrow[HNCO]{NH_2COCl\ or} \text{ammelide}$$

Such a reaction mechanism utilizes the fact (p. 573) that carbamyl chloride dissociates at a fairly low temperature into *iso*cyanic acid. Dyson [7] has criticized this mechanism in favor of the simpler reaction:

$$NH_2COCl\ (\text{from } COCl_2) + 2NH_3 \longrightarrow NH_2CONH_2 + NH_4Cl,$$

but he has failed to provide a satisfactory explanation for the low yield of urea.

Similarly, although urethane and ammonia interact to form urea, it is not in the simple manner of "ester + NH_3". In fact, in the cold (25°) there is no evidence of reaction [8] after 10 months. Here again, urea formation depends on the pyrolysis of ethyl urethane into *iso*cyanic acid, a reaction which actually occurs by refluxing. Thus, in two hours' time, there results a 16 percent yield of cyanuric acid from ethyl urethane:

$$3NH_2{-}CO{-}OC_2H_5 \longrightarrow (HNCO)_3 + 3C_2H_5OH.$$

Thus far, at least, no general method has been developed to produce *iso*cyanates from substituted urethanes, but methyl *p*-benzoylphenylurethane [9] easily changes into *p*-benzoylphenyl *iso*cyanate by fusion at 155° in a retort:

$$C_6H_5CO{-}C_6H_4{-}NH{-}CO_2CH_3 \longrightarrow CH_3OH + C_6H_5CO{-}C_6H_4{-}N{=}C{=}O.$$

Betulin-phenylurethane, $C_{30}H_{48}(O{-}CO{-}NHC_6H_5)_2$, produces a sublimate [10] of *symmetrical* diphenyl urea at 195°, and at 310°, carbon dioxide may be detected.

Ammonium thiocyanate undergoes rearrangement into thiourea by heating, and undoubtedly the mechanism for this reaction is the same as the preceding. The salt melts at 150°, and further heating [11] produces not only thiourea, but also guanidine, melamine and melam ($C_6H_9N_{11}$). The yield of the latter depends on speed of heating and high temperature. At 182°, the equilibrium mixture consists [12] of 77.6-78 percent

[7] Dyson, *Chem. Reviews* **4**, 136 (1927).
[8] Werner, *J. Chem. Soc.* **113**, 622 (1918).
[9] Dinglinger, *Ann.* **311**, 130 (1900).
[10] Vesterberg and Vesterberg, *Arkiv. Kemi. Mineral. Geol.* **9**, No. 27, 17 pp. (1926); *Chem. Abstracts* **20**, 1995 (1926).
[11] Waddell, *J. Phys. Chem.* **2**, 534 (1898); Liebig, *Ann.* **10**, 10 (1834).
[12] Burrows, *J. Am. Chem. Soc.* **46**, 1623 (1924)

thiocyanate and the remainder thiourea. Melem, $C_6H_6N_{10}$, is formed [13] from ammonium thiocyanate at 260°.

Pyrolysis of Urea.

Above its melting point (132°) urea dissociates into ammonia and an equilibrium mixture [14] of cyanic acid:

$$HNCO \rightleftharpoons HOCN.$$

If dry, no carbon dioxide is produced. Therefore, ammonium cyanate has a chance to be formed, and this is practically an exclusive sublimation product [15] when urea is heated at 160-180° in a vacuum. In fact, it is pointed out that if Wöhler had purified his synthetic urea by vacuum distillation, his epoch-making discovery might never have been made.

Since only a part of the urea is decomposed at its melting point, there is also the chance of biuret formation by the addition of one mol of *iso*cyanic acid to one of urea. To be sure, the yields of biuret by this procedure are poor, yet this constitutes the laboratory method that is almost universally recommended to beginning students. Where color reactions only are desired, this method of synthesis is satisfactory. The equation usually given to represent its formation is:

$$2CO(NH_2)_2 \longrightarrow NH(CONH_2)_2 + NH_3,$$

but it is more in keeping with facts to represent this reaction by two steps:

$$HN{=}C(OH)NH_2 \longrightarrow HNCO + NH_3$$

$$HN{=}C(OH)NH_2 + HNCO \longrightarrow HN(CONH_2)_2 \quad \left(\begin{smallmatrix}or\ enol\\ isomer\end{smallmatrix}\right)$$

Biuret also is unstable to heat. It undergoes two reactions; one of deammonation [16] and one of dehydration.[17] In the latter reaction, tricyanourea, $(NH_2{-}CO{-}NHCN)_3$, is formed and in the former, a decomposition which occurs above its melting point, 190°, ammonia and cyanic acid (cyanuric acid) result. Of course, the usual mixture of products from the interaction of ammonia and cyanic acid also appear in the reaction mixture. Good yields of biuret [18] may be formed at 130° if urea hydrochloride is heated instead of urea. The reason for the better yield obviously lies in the fact that the ammonia which is liberated combines with hydrogen chloride instead of with HNCO.

[13] Klason, *J. prakt. Chem.* [2] **33**, 287 (1886).
[14] Werner, *J. Chem. Soc.* **103**, 1010 (1913).
[15] Escales, *Chem. Ztg.* **35**, 595 (1911).
[16] Werner, *J. Chem. Soc.* **103**, 1015 (1913); Fearon, *Physiol. Reviews* **6**, 411 (1926).
[17] Hantzsch and Bauer, *Ber.* **38**, 1013 (1905).
[18] Werner, *loc. cit.* p. 1015; Schiff, *Ber.* **29**, 298 (1896); *Ann.* **299**, 236 (1898); Hofmann, *Ber.* **4**, 262 (1871).

Wiedemann discovered biuret by heating urea nitrate. Furthermore, he noted [19] that it could be formed from urea alone at 150-170°.

Since both urea and biuret undergo pyrolysis into cyanuric acid, this becomes a method of synthesis for the latter compound. If 100 grams of urea is heated [20] in a porcelain dish by means of a sand bath or an oil bath, the substance fuses at about 130°. It is then gradually heated to 200°, when the melt is cooled and repeatedly extracted with hot water. Twelve grams of tricyanourea remains undissolved, and 35 grams of cyanuric acid is extracted by the water.

Davis and Underwood [21] have utilized urea as a source of nascent *iso*cyanic acid in the production of phenylurea from aniline:

$$C_6H_5NH_2 + HNCO \longrightarrow C_6H_5NH{-}CONH_2.$$

To accomplish this step, a mixture of aniline and urea is heated at 160°, a temperature at which urea is known to dissociate. Ammonia is evolved. However, the reaction does not stop at this point since phenylurea also dissociates. The phenyl *iso*cyanate, thus formed, unites with more aniline, giving *symmetrical* diphenyl urea. The following reaction, then, is general:

$$HN{=}C(OH)NH_2 + 2C_6H_5NH_2 \longrightarrow CO(NHC_6H_5)_2 + 2NH_3.$$

Phenylurea and diphenyl-urea may be prepared in good yields (53 percent and 90 percent respectively) by boiling [22] a mixture of urea, aniline hydrochloride and water.

Substituted Ureas.

Monoethyl urea gives only a trace of ethyl amine [23] by heating, but yields ammonia and diethyl cyanurate instead. Although only one of the two possible courses of decomposition seems to be taken in this pyrolysis, they are both appropriated when monophenyl-urea is heated for 2 hours at 160° since 77 percent of the theoretical yield of diphenylurea [24] is formed. The following equations explain this result:

$$C_6H_5NH{-}CONH_2 \rightleftharpoons C_6H_5N{=}C{=}O + NH_3$$

$$C_6H_5NH{-}CONH_2 \rightleftharpoons C_6H_5NH_2 + HNCO$$

$$\downarrow$$

$$(C_6H_5NH)_2CO$$

[19] Wiedemann, *Ann.* **68**, 324 (1848).
[20] Hantzsch and Bauer, *Ber.* **38**, 1010 (1905).
[21] Davis and Underwood. *J. Am. Chem. Soc.* **44**, 2595 (1922).
[22] Davis and Blanchard, *ibid.* **45**, 1816 (1923).
[23] Werner, *J. Chem. Soc.* **105**, 923 (1914).
[24] Davis and Underwood, *loc. cit.* p. 2601.

Davis and Blanchard have demonstrated that disubstituted ureas, either symmetrical or unsymmetrical, "dearrange" in but one way:

Unsymmetrical:

$$R_2N{-}CONH_2 \rightleftharpoons R_2NH + HNCO$$

Symmetrical:

$$CO(NHR)_2 \rightleftharpoons RNH_2 + RNCO\,.$$

In fact, an odor of phenyl *iso*cyanate may be distinguished [25] when carbanilide is heated on a platinum foil a little above its melting point. No efficient scheme has as yet been devised to prepare phenyl *iso*cyanate by this method, but it may be captured by a reactive compound. Eckenroth and Wolf used salol for this purpose:

$$CO(NHC_6H_5)_2 + C_6H_4\!<\!\begin{matrix}OH\\CO_2C_6H_5\end{matrix} \longrightarrow C_6H_5NH_2 + C_6H_4\!<\!\begin{matrix}O{-}CONHC_6H_5\\CO_2C_6H_5\end{matrix}$$

Symmetrical ethylphenylurea [26] gives off ethyl amine to form an 80 percent yield of symmetrical diphenylurea, by heating 90 minutes at 160-170°. Similarly, in three hours at this temperature, 2 grams of monobenzylurea changes into dibenzylurea ("dibenzyl" is the name in the reference) so that 0.6 gram of it may be isolated in the pure state.

Methyl chloride is evolved [27] when the hydrochloride of *O*-methylurea is heated above its melting point, 130°:

$$HN{=}C(OCH_3){-}NH_2.HCl \longrightarrow NH{=}C(OH){-}NH_2 + CH_3Cl\,.$$

Acetyl-urea [28] may be sublimed in part at 180-190°, but further heating induces a complete decomposition into cyanuric acid and acetamide:

$$HN{=}C(OH){-}NH{-}COCH_3 \longrightarrow HNCO + CH_3CONH_2$$

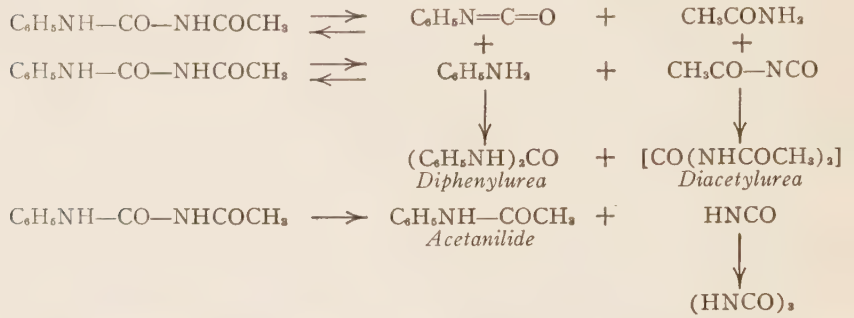
$$\downarrow$$

$$(HNCO)_3$$

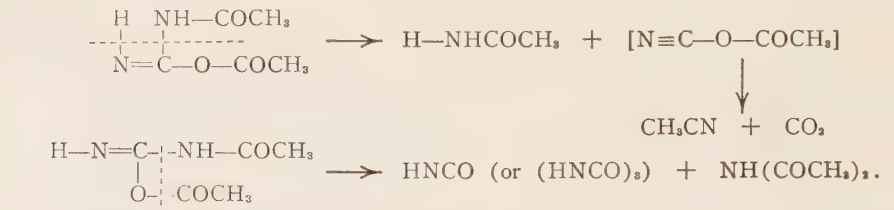
Methyl acetyl-urea [29] behaves similarly and gives fair yields of methyl *iso*cyanate above 180°. There is a rather complex reaction in this case, however, for further heating also liberates not only acetamide but also carbon dioxide, ammonia, methyl amine, *N*-methylacetamide, *N,N'*-dimethyl- and *N,N',N''*-trimethyl-*iso*cyanuric acid. From these two cases, it might appear reasonable that phenyl *iso*cyanate should result from the pyrolysis of phenyl-acetyl-urea, but preliminary experiments [30] indicate that the yield of phenyl *iso*cyanate by such a method is very

[25] Eckenroth and Wolf, *Ber.* **26**, 1467 (1893).
[26] Davis and Blanchard, *J. Am. Chem. Soc.* **45**, 1819 (1923).
[27] Stieglitz and McKee, *Ber.* **33**, 811 (1900); McKee, *Am. Chem. J.* **26**, 246 (1901).
[28] Datta and Gupta, *J. Am. Chem. Soc.* **35**, 1893 (1913).
[29] Hofmann, *Ber.* **14**, 2727 (1881).
[30] Smith, in the author's laboratory; unpublished results.

small. The two chief products, when the decomposition is performed at 265° for one hour, are symmetrical diphenyl urea (12.3 grams from 20 grams) and acetanilide (2.7 grams from 20 grams). This is similar to the formation of diphenylurea from phenylurea (above), and a similar series of reactions may be used to explain the result:



Diacetylurea [31] is known to break in two ways at 170°; one leads to acetamide and the other to diacetamide:



The esters of allophanic acid all decompose [32] a few degrees above their melting points, changing into cyanic acid, cyanuric acid and the corresponding alcohol providing it is not a tertiary alcohol. In case the alkyl of the allophanate is derived from a tertiary alcohol, this appears as an olefine following the pyrolysis. Grandière recommends this as a good test for tertiary alcohols.

Carbamazide, hydroxyurea and their monosubstituted analogs are derivatives of urea which may well be discussed at this point. From the standpoint of urea chemistry there is nothing spectacular about them since their pyrolysis proceeds in the normal way through the *iso*cyanate step. From the standpoint of azide chemistry, or hydroxamic acid chemistry, however, their behavior is extremely spectacular inasmuch as they cannot be made to participate in rearrangements of the Curtius or Lossen type. In this respect they differ from all compounds

[31] Werner, *J. Chem. Soc.* **109**, 1120 (1916).
[32] Grandière, *Bull. soc. chim.* **35**, 187 (1924).

with the —CO—N_3 or the —CO—NHOH groups. Thus, the rearrangement of azides to *iso*cyanates:

$$R—CO—N=N\equiv N \longrightarrow N_2 + R—N=C=O,$$

in which the radical R, originally attached to carbon, becomes ultimately attached to nitrogen has no parallel in carbamazide or in monosubstituted carbamazides. Were it to behave in this manner, carbamazide should give hydrazine, and phenylcarbamazide should produce phenylhydrazine, but no traces of these compounds are met in practice. From this evidence, the inference has been drawn [33] that these compounds possess the "urea structure" and not the "carbamate structure". Carbamazide, therefore, is HN=C(OH)—N_3 and not NH_2—CO—N_3; hydroxyurea is HN=C(OH)—NHOH and not NH_2—CO—NHOH. With this structure, these compounds are neither acid-azides nor hydroxamic acids; therefore, rearrangement to the hydrazines should not necessarily be anticipated.

From 5 grams of carbamazide,[34] heated at 120°, 800 cc. of nitrogen, 1.1 grams of hydrazoic acid and 2 grams of a solid residue are formed. In this residue are to be found ammonium azide, urazole and 0.37 gram of cyanuric acid. This pyrolysis occurs also in boiling toluene or xylene.

$$HN=C\begin{matrix}<^{N_3}\\ _{O—H}\end{matrix} \longrightarrow HNCO + HN_3$$

$$3HNCO \longrightarrow (HNCO)_3$$

$$4HN_3 \longrightarrow NH_4N_3 + 4N_2$$

Unquestionably, part of the nitrogen which is formed is eliminated directly, with the formation of what Curtius [35] terms a "rigid residue"; i.e., either [HN=C(OH)—N=] or [H_2N—CO—N=]. This univalent nitrogen radical may react with aromatic hydrocarbons if it is formed in their presence; thus, benzene accepts it to form phenylurea. It may double itself to form H_2N—CO—N=N—CO—NH_2, or it may combine with *iso*cyanic acid to form urazole. This is probably the source of the urazole mentioned above. Except for the fact that two nitrogen atoms are united in the final product, there is no reason to believe that a "rearrangement" is the precursor of urazole. Instead:

$$NH_2—CO—N= + HNCO \longrightarrow \begin{matrix}NH—NH\\ |\quad\ |\\ CO\quad CO\\ \diagdown\ \diagup\\ NH\end{matrix}$$

[33] Hurd and Spence, *J. Am. Chem. Soc.* **49**, 266 (1927).
[34] Curtius and Schmidt, *J. prakt. Chem.* **105**, 177 (1923).
[35] Curtius, *Ber.* **56**, 1577 (1923).

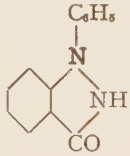
Hydroxyurea has not been subjected to experiments on thermal decomposition, but the related compound, phenylhydroxyurea,[36] changes into carbanilido-phenylhydroxyurea by refluxing in alcohol. It was shown definitely that phenyl *iso*cyanate is not liberated as such in this process, although it might be liberated by more vigorous heating in the absence of a solvent, a detail which has not been investigated. The equation for its decomposition in solution is:

$$2C_6H_5NH{-}CO{-}NHOH \text{ (or the enol)} \longrightarrow NH_2OH + C_6H_5NH{-}CO{-}NH{-}O{-}CONHC_6H_5.$$

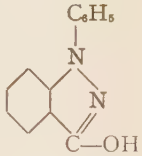
The disubstituted carbamazides, $R_2N{-}CO{-}N_3$, and the disubstituted hydroxyureas, $R_2N{-}CO{-}NHOH$, are correctly represented in their chemical behavior by the formulas given. They undergo the Curtius or the Lossen rearrangements, when heated, giving compounds related to hydrazines. No dialkylcarbamazides are known as yet, but diphenylcarbamazide decomposes almost quantitatively[37] into phenyl-1-oxy-3-indiazene in accordance with the following equation when it is refluxed for a 3 hours in tetralin or in xylene; see page 684.

$$(C_6H_5)_2N{-}CO{-}N{=}N_2 \longrightarrow N_2 + [(C_6H_5)_2N{-}CO{-}N{=}]$$

$$\longrightarrow (C_6H_5)_2N{-}N{=}C{=}O \longrightarrow$$



or



α,α-Diethyl-β-hydroxyurea[38] undergoes pyrolysis in a vacuum of 25 mm. when the temperature of the heating bath reaches 150-160°. Evidently carbonyl-diethylhydrazine is formed, because an alkaline solution causes it to evolve diethylhydrazine. The equations follow:

$$(C_2H_5)_2N{-}CO{-}NHOH \longrightarrow (C_2H_5)_2N{-}NCO + H_2O$$

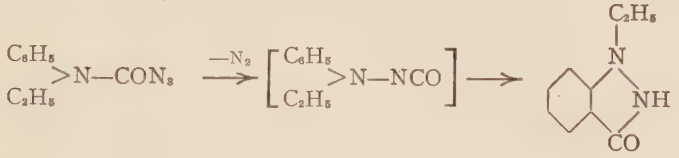
$$(C_2H_5)_2N{-}NCO \xrightarrow{2NaOH} (C_2H_5)_2N{-}NH_2 + Na_2CO_3.$$

Diphenyl-hydroxyurea, $(C_6H_5)_2N{-}CO{-}NHOH$, melts with slight decomposition[39] at 134°; at 150°, the decomposition becomes vigorous, presumably with the formation of carbonyl-diphenylhydrazine, $(C_6H_5)_2N{-}NCO$. At least, derivatives of the original compound such as $(C_6H_5)_2N{-}CO{-}NNa{-}OCOCH_3$, rearrange quickly to diphenyl-hydrazine even in cold water solution.

When methyl phenyl carbamyl azide is heated for 6 hours in xylene,

[36] Kjellin, *Ber.* **26**, 2384 (1893). Hurd, *J. Am. Chem. Soc.* **45**, 1483 (1923).
[37] Stollé, *Ber.* **57**, 1063 (1924); *J. prakt. Chem.* **117**, 185 (1927).
[38] Hurd and Spence, *J. Am. Chem. Soc.* **49**, 271 (1927).
[39] Hurd, *ibid.* **45**, 1485 (1923).

1-methyl indazolone is formed.[40] Similarly, 19 grams of ethyl phenyl carbamyl azide gives rise to 11 grams of 1-ethyl indazolone after heating for 3 hours in xylene:



Methyl *o*-tolyl-carbamazide (25 grams) changes by heating into 1,7-dimethyl-indazolone (6 grams), but there is also formed the dimer of the *iso*cyanate (2.7 grams), $(o\text{-}CH_3C_6H_4\text{—}N(CH_3)\text{—}NCO)_2$.

Thioureas. We may pass rapidly over this topic since thiourea and urea are similar in many respects in their reactions of pyrolysis. The former breaks down reversibly into ammonia and *iso*thiocyanic acid, HNCS, just as the latter decomposes into ammonia and *iso*cyanic acid, HNCO. Thiourea is formed in good yields when ammonium thiocyanate [41] is heated for 2 hours by an oil bath at 170°. It was demonstrated by Claus [42] that the salt need not be highly purified at the outset, and that the thiourea could be prepared in an enameled-iron apparatus over a free flame. At a little higher temperature (180-190°) the odor of carbon disulfide appears, and if dry ammonium thiocyanate (or thiourea) is heated in a retort [43] for 20 hours at this temperature, guanidine thiocyanate may be isolated from the residue. This is undoubtedly due to a twofold dissociation of thiourea:

$$HN{=}C(SH)\text{—}NH_2 \longrightarrow HN{=}C{=}NH + H_2S$$
$$HN{=}C(SH)\text{—}NH_2 \longrightarrow NH_3 + H\text{—}N{=}C{=}S$$

and then:

$$HN{=}C{=}NH + NH_3 \longrightarrow \underset{\textit{Guanidine}}{NH{=}C(NH_2)_2}.$$

Melam and carbon disulfide become important pyrolytic products (Claus) between 200-300°:

TABLE LVI.. *Pyrolysis of Ammonium Thiocyanate.*

Ammonium Thiocyanate (NH_4SCN) Grams	Hours Heated	Temperature °C.	Melam Grams	Carbon Disulfide Grams
200	18	200	30	28
200	12	250	34	31
200	5	300	42	40

[40] Stollé, Nieland and Merkle, *J. prakt. Chem.* 116, 192 (1927).
[41] Reynolds, *Ann.* 150, 227 (1869).
[42] Claus, *Ann.* 179, 113 (1875).
[43] Volhard, *J. prakt. Chem.* [2] 9, 15 (1874); *Ber.* 7, 92 (1874).

The kinetics of the rearrangement of ammonium thiocyanate into thiourea has been studied by Kappema [44] at 10° intervals between 140-180°; the reaction is shown to be reversible and of the first order. The percentage of thiourea at equilibrium is shown in Table LVII.

TABLE LVII. *Yield of Thiourea at Equilibrium Temperatures.*

Temperature °C.	Thiourea Percent
140	28.10
150	26.24
160	24.56
170	23.09
180	21.76

When either thiourea or ammonium thiocyanate [45] is heated at 160° with aniline (or with aniline hydrochloride), phenyl-thiourea and symmetrical-diphenyl-thiourea, $CS(NHC_6H_5)_2$, are formed. Heating phenyl-thiourea causes two effects, namely, the change to aniline and *iso*thiocyanic acid, or to ammonia and phenyl *iso*thiocyanate. These transformations occur at 160°:

$$C_6H_5NH{-}CS{-}NH_2 \longrightarrow C_6H_5NH_2 + HNCS$$

$$+$$

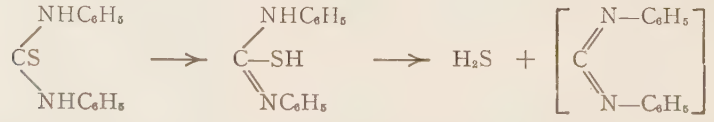
$$C_6H_5NH{-}CS{-}NH_2 \longrightarrow C_6H_5NCS + NH_3$$

$$\downarrow\uparrow$$

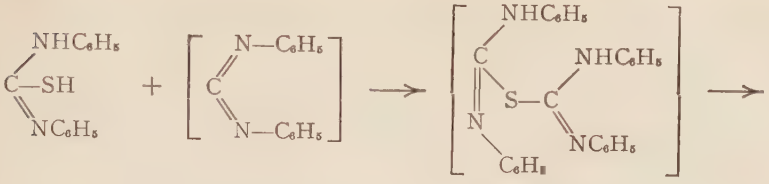
$$CS(NHC_6H_5)_2$$

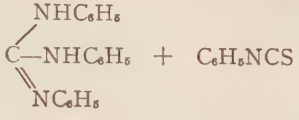
Thiocarbanilide (0.8 gram from 3 grams of phenylthiourea) is formed, as indicated. Hydrogen sulfide is also evolved. Thiocarbanilide dissociates at the distillation temperature into aniline and phenyl *iso*-thiocyanate, but of course these substances recombine on cooling. Substances with offensive odors also result during the distillation.

Naunton believes [46] that the following mechanism is the one which is most satisfactory to explain the formation of triphenyl guanidine during the pyrolysis of thiocarbanilide:



[44] Kappema, *Quart. J. Indian Chem. Soc.* **4**, 217 (1927); *Chem. Abstracts* **21**, 3526 (1927).
[45] Davis and Underwood, *J. Am. Chem. Soc.* **44**, 2597 (1922).
[46] Naunton, *J. Soc. Chem. Ind.* **45**, 34T (1926).





Triphenyl guanidine *Phenyl isothiocyanate*

At the melting point (79°) of *S*-methyl-thiourea,[47] methyl mercaptan is produced in good yields. This method of synthesis for *methyl mercaptan* is recommended as an excellent one:

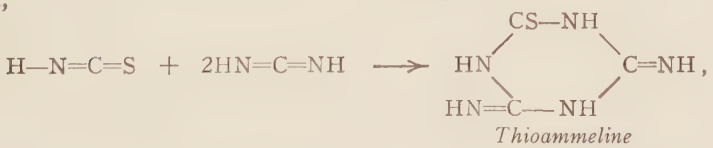
$$CH_3S{-}C(NH_2){=}NH \longrightarrow CH_3SH + [HN{=}C{=}NH]$$
$$2\,[HN{=}C{=}NH] \longrightarrow NH{=}C(NH_2){-}NHCN.$$

Somewhat resembling this is the smooth formation [48] of ethyl mercaptan and cyanuric acid from *S*-ethyl thiocarbamate, $NH_2{-}CO{-}SC_2H_5$ or $HN{=}C(OH){-}SC_2H_5$, at 150° in a sealed tube.

At 195°, acetyl-thiourea [31] pyrolyzes into acetamide and other products:

$$HN{=}C(SH){-}NH{-}COCH_3 \longrightarrow H_2N{-}COCH_3 + [HNCS]$$
$$2\,[HNCS] \longrightarrow CS_2 + CN{-}NH_2 \text{ or } HN{=}C{=}NH.$$

Then,



Thioammeline

The great instability of formamidine-disulfide, $\left(\begin{matrix}-S-C=NH\\ \quad\quad |\\ \quad\quad NH_2\end{matrix}\right)_2$, has been mentioned on page 586. It decomposes spontaneously into sulfur, cyanamide and thiourea.

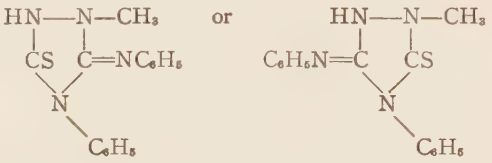
The hydrochloride of methyl-phenyl-thiosemicarbazide melts at 120° and evolves hydrogen sulfide [49] in so doing. It resolidifies at 130° and

[47] Arndt, with Milde and Eckert, *Ber.* **54**, 2236 (1921).
[48] Pinner, *Ber.* **14**, 1083 (1881).
[49] Marckwald and Sedlaczek, *Ber.* **29**, 2921 (1896).

remelts at 230°. A triazole derivative has been formed, in accordance with the following equation:

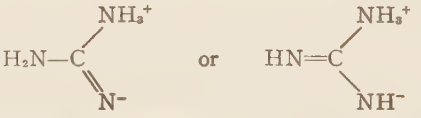
$$2C_6H_5NH{-}CS{-}NH{-}NH{-}CH_3\cdot HCl \longrightarrow H_2S + CH_3NH{-}NH_3Cl + C_{15}H_{14}N_4S\cdot HCl.$$

The base $C_{15}H_{14}N_4S$ is either

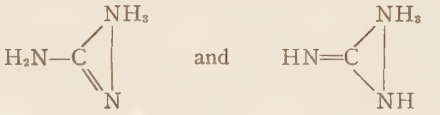


Guanidine and Related Compounds.

Usually, guanidine is assigned the structure $HN{=}C(NH_2)_2$. Lecher and Graf [50] believe that it is more properly represented as either



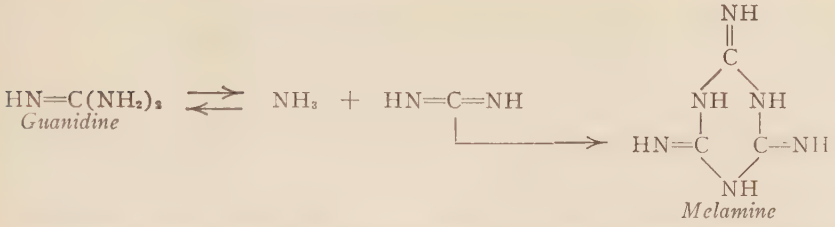
and that presumably these two forms are in equilibrium. Krall [51] had previously reached the same conclusion, assigning for it the tautomeric formulas,



In support of this formula it may be stated that nitrous acid liberates only enough nitrogen to be accounted for by one of the three nitrogens.

Guanidine decomposes (Krall) at about 160° with a brisk evolution of ammonia. The dry, solid mass melts, and then resolidifies at once in the form of melamine. Much the same type of pyrolysis may be secured with guanidine carbonate, a compound much more easily obtained than guanidine itself. When this is heated strongly [52] in a test-tube, ammonia is given off and cyanamide may be detected in the residue by testing with ammoniacal silver nitrate. When it is heated in a sublimation apparatus, the first portions of the sublimate contain considerable guanidine carbonate, whereas the latter portions consist almost entirely of melamine, the tri-mer of cyanamide:

[50] Lecher and Graf, *Ann.* **438**, 154 (1924).
[51] Krall, *J. Chem. Soc.* **107**, 1396 (1915).
[52] Davis and Underwood, *J. Am. Chem. Soc.* **44**, 2603 (1922).



Guanidine differs from urea and thiourea in being quite non-reactive with aniline at high temperatures.

Biguanide, $H_2N—C(NH)—NH—C(NH)—NH_2$, the analog of biuret, is formed [53] when guanidine hydrochloride (1 gram) is heated for 3 or 4 minutes at 180-185°.

α-Nitroguanidine, on heating above its melting point,[54] gives some β-nitroguanidine along with the expected dearrangement products, or the products of their decomposition and interaction, namely, cyanic acid, cyanuric acid, cyanogen, urea, *para*cyanogen, cyanamide, melamine, ammeline, ammelide, melam and mellon. The initial step in this process is a pyrolysis either into nitroamide and cyanamide, or into ammonia and nitrocyanamide.

An intermediate stage in the change from thiocarbanilide into triphenylguanidine (p. 614) was assumed to be carbodiphenylimide, $C(=NC_6H_5)_2$. This compound and aniline are formed [55] when triphenylguanidine is subjected to pyrolysis:

$$C_6H_5N=C(CHC_6H_5)_2 \longrightarrow C_6H_5N=C=NC_6H_5 + C_6H_5NH_2.$$

This reaction is perfectly similar to the formation of carbon dioxide from carbonic acid, or of *iso*cyanic acid from urea, or in fact of ketene from acetone.

Much in the way that urea may be made to serve as a source of nascent *iso*cyanic acid (p. 608), so also substituted guanidines act as a source of a nascent carbo-dianil, $C(=NAr)_2$, when heated with amines.[56] Thus, *unsymmetrical*-triphenylguanidine, or diphenylguanidine, in reaction with aniline produces *symmetrical*-triphenylguanidine:

$$HN=C\begin{cases}NH—C_6H_5 \\ NH—C_6H_5\end{cases} \rightleftharpoons \begin{cases}C_6H_5NH_2 + [C_6H_5N=C=NH] \\ NH_3 + [C_6H_5N=C=NC_6H_5]\end{cases}$$

With aniline, $C_6H_5N=C=NH$ would regenerate diphenylguanidine, but $C_6H_5N=C=NC_6H_5$ would form triphenylguanidine, $C_6H_5N=$

[53] Bamberger and Dieckmann, *Ber.* **25**, 543 (1892).
[54] Davis and Abrams, *Proc. Am. Acad. Arts Sci.* **61**, 437 (1926); *Chem. Abstracts* **21**, 1968.
[55] Merz and Weith, *Z. Chem.* **1870**, 74.
[56] Klinger, *Z. physiol. Chem.* **155**, 206 (1926).

$C(NHC_6H_5)_2$. Similarly, $HN{=}C{<}^{N(C_6H_5)_2}_{NHC_6H_5}$ may give diphenylamine and $C_6H_5N{=}C{=}NH$, which in the presence of aniline would change into diphenylguanidine. In turn, the latter would then change into *symmetrical*-triphenylguanidine in the manner just indicated. The presence of an excess of amine does not alter the facts of the pyrolysis, but it does change the equilibrium. Other *symmetrical* trisubstituted guanidines have been synthesized by an application of this method.

Preparation of Isocyanates by Methods of Pyrolysis.

In the preceding pages this subject has been approached in a number of instances. Frequently, mention has been made of the formation of cyanuric acid from many varied types of urea derivatives as well as the depolymerization of cyanuric acid at high temperatures. Other cases include:

Oxanilic acid chloride into phenyl *iso*cyanate (good yields); p. 571.
Phenylcarbamyl chloride into phenyl *iso*cyanate (good yields); p. 574.
Methyl acetylurea into methyl *iso*cyanate; p. 609.
Methyl *p*-benzoylphenylurethane into *p*-benzoylphenyl *iso*cyanate; p. 606.
Carbanilide, or phenylacetyl urea, into phenyl *iso*cyanate; pp. 609, 610.
Acid azides into *iso*cyanates; a general reaction, which will be discussed in more detail in a later chapter.
Phenyl thiourea, and diphenylthiourea, into phenyl *iso*thiocyanate; p. 614.
A substituted urethane, $C_6H_5CH{=}N{-}NH{-}CO{-}O{-}C_6H_4OCH_3$, into the dimer of $C_6H_5CH{=}N{-}N{=}C{=}O$; p. 643.

Carbanil-dibromide, which is made from phenyl *iso*cyanate and bromine in chloroform solution, melts at 144°; when quickly heated [57] above 140° it changes into *p*-bromophenyl*iso*cyanate:

$$C_6H_5{-}N{=}COBr_2 \longrightarrow HBr + Br{-}C_6H_4{-}N{=}C{=}O.$$

This method is interesting, but it does not offer a solution to the problem of *iso*cyanate synthesis since an *iso*cyanate was taken at the outset. The orienting influences of the $-N{=}C{=}O$ group to *para* is interesting.

Nitrosomethyl-urea [58] melts at 121°, and in so doing decomposes into trimethyl cyanurate:

$$3CH_3{-}\underset{\underset{NO}{|}}{N}{-}\overset{\diagdown\ \diagup}{C}{=}NH \longrightarrow 3N_2 + (CH_3NCO)_3 + 3H_2O.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

Methyl *iso*cyanate undergoes an interesting change [59] as it is slowly passed through a tube filled with glass beads and heated to faint redness. The product of the reaction is methylaminoformyl cyanide, and

[57] Curtius, *J. prakt. Chem.* **87**, 513 (1913).
[58] Werner, *J. Chem. Soc.* **115**, 1093 (1919).
[59] Slotta and Tschesche, *Ber.* **60**, 1022 (1927).

this in turn changes into methyl *iso*cyanate and hydrogen cyanide on dry distillation:

$$CH_3NH—CO—CN \longrightarrow CH_3NCO + HCN.$$

Anschütz [60] has prepared ethyl *iso*cyanate by a novel plan. By the interaction of carbon oxysulfide and an amine, a thiocyanate is formed, which is then converted to the dry mercuric salt, and the latter is pyrolyzed at 160-165°. Thus:

$$2C_2H_5NH_2 + COS \longrightarrow C_2H_5NH—CO—S—NH_3C_2H_5$$

Ethylammonium ethylthiolcarbamate,

$$C_2H_5NH—CO—S\cdot NH_3C_2H_5 + HgCl_2 \longrightarrow C_2H_5NH—CO—S—HgCl + C_2H_5NH_3Cl$$

$$3C_2H_5NH—CO—S—HgCl \longrightarrow 2C_2H_5N=C=O + C_2H_5NH_3Cl + Hg_3S_2Cl_2 + COS.$$

From 25 grams of ethylammonium ethylthiolcarbamate, 48 grams of the compound, $C_2H_5NH—CO—S—HgCl$ is isolated, 44 grams of which yield 4.5 grams of pure ethyl *iso*cyanate. *Iso*butyl *iso*cyanate is prepared by an exactly analogous process. The equations for the pyrolysis of other mercury salts related to these are given also.

$$(R—NH—CO—S—)_2Hg \xrightarrow{\text{heat}} HgS(red) + COS + CO(NHR)_2$$

Mercuric alkylthiolcarbamate, (R = ethyl, or *iso*butyl.)

$$(R—NH—CS—S—)_2Hg \longrightarrow HgS(black) + CS_2 + CS(NHR)_2$$

and also $(R—NH—CS—S—)_2Hg \longrightarrow HgS + H_2S + 2R—NCS$

Mercuric alkyldithiocarbamate

$$3RNH—CS—S—HgCl \xrightarrow{160\text{-}165^\circ} Hg_3S_2Cl_2 + 2RNCS + RNH_3Cl + CS_2.$$

If methyl thiocyanate [61] is heated at 180-185°, much of it rearranges into methyl *iso*thiocyanate. There is also a crystalline residue which indicates a trimer.

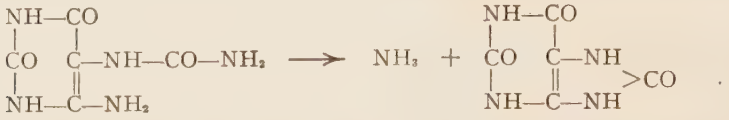
Thermal Decomposition of Ureas, the Course of Which Varies from Simple Ureas because of the Presence of an Active Substituent Group.

This type of pyrolysis is usually characterized by ring closures. At 227°, carbonyl diurea [62] changes into cyanuric acid by the loss of a molecule of ammonia:

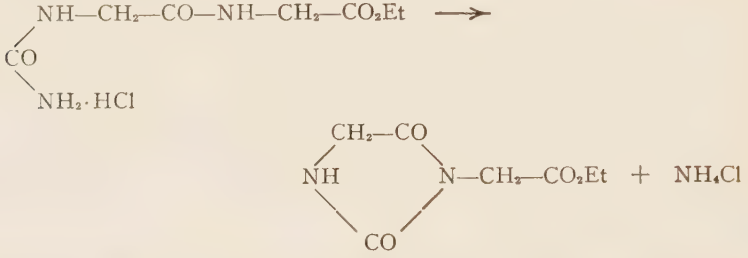
$$CO(NH—CONH_2)_2 \longrightarrow NH_3 + CO\langle \begin{matrix} NH—CO \\ NH—CO \end{matrix} \rangle NH.$$

[60] Anschütz, *Chem. Ztg.* **34**, 89 (1910); *Ann.* **359**, 211 (1908).
[61] Hofmann, *Ber.* **13**, 1349 (1880).
[62] Walters and Wise, *J. Am. Chem. Soc* **39**, 2474 (1917).

At about the same temperature, 5-carbamido-4-amino-2,6-dioxypyrimidine [63] also loses ammonia, forming uric acid.



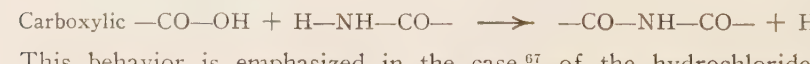
By heating ethyl carbamideglycylglycinate hydrochloride [64] for an hour *in vacuo* at 180-190°, ammonium chloride is detached as ethyl hydantoin-3-acetate is formed:



The transformation of *o*-amino-phenylurea [65] into phenylene-urea takes place at 150°:

An *o*-phenolic group will also participate in this type of ring closure; witness, for example, the deammonation [66] of 4-nitro-2-hydroxy-phenylurea (4.2 grams) into nitrobenzoxazolone (1.5 grams after recrystallization):

This preferential elimination of ammonia between an amide group and a phenolic group is quite at contrast with the result when the amide group is reacting with a carboxyl (cf. pp. 597-601):



This behavior is emphasized in the case [67] of the hydrochloride of guanidino-acetic acid (glycocyamin), which slowly changes into the

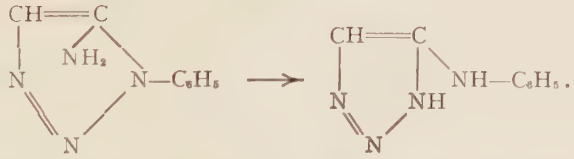
[63] Traube and others, *Ann.* **432**, 266 (1923).
[64] Gränacher and Landolt, *Helv. Chim. Acta* **10**, 799 (1927).
[65] Pellizzari, *Gazz. chim. ital.* **49**, I, 16 (1919).
[66] Semper and Lichtenstadt, *Ann.* **400**, 302 (1915).
[67] Strecker, *Compt. rend.* **52**, 1212 (1861); Nicola, *Chem. Zentr.* **1902**, II, 296; Korndörfer, *Archiv der Pharmazie* **242**, 620 (1904).

hydrochloride of 2-imino-4-keto-imidazol-tetrahydride (glycocyamidin) at 160-170°:

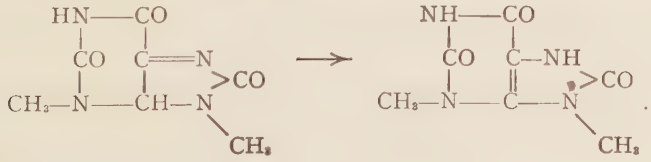
The relationship between creatine and creatinine, the *N*-methyl homologs of these substances, is a similar one. The thermal decomposition of β-hydroxyethyl-urea [68] leads to the formation of the inner anhydride of β-hydroxyethyl-carbamic acid. In practice, β-hydroxyethylamine reacts with *iso*cyanic acid, and this addition compound is distilled.

In the two isomeric pyrazole-carboxamides which are formulated below, the change [69] from the first into the second occurs at 133°, the melting point. After melting, the material resolidifies to remelt at 142°, the melting point of the second compound. Apparently, a phenyl group wanders in this transformation:

The rearrangement [70] of 1-phenyl-5-aminotriazole into 5-anilino-triazole takes place at 145°:

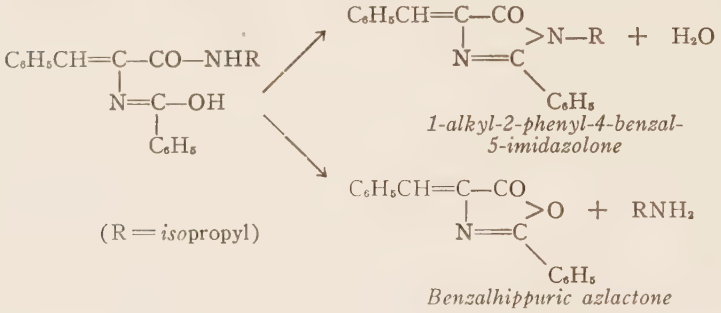


Another instance of rearrangement in *N*-heterocyclic compounds which may be taken up here is that of 3,9-dimethyl-$\Delta^{5,7}$-*iso*uric acid [71] into 3,9-dimethyl uric acid at a temperature of 310-320° for 10 minutes:



[68] Knorr and Rössler, *Ber.* **36**, 1278 (1903).
[69] von Auwers and Ottens, *Ber.* **58**, 2072 (1925).
[70] Dimroth, *Ann.* **364**, 215 (1908).
[71] Biltz and Krzikalla, *Ann.* **457**, 131 (1927).

The pyrolysis of benzoyl-*α*-aminocinnamic benzylamide and related compounds, $C_6H_5CH{=}C(NH{-}COC_6H_5){-}CO{-}NHR$, suggests that the formula possesses the enol structure. There appear to be two types of change,[72] depending on the group R; when it is methyl or benzyl, water is eliminated. by heating thereby producing an imidazolone, but when it is a secondary group such as *iso*propyl the amine is eliminated giving an azlactone. Both types of reaction are produced by vacuum heating for an hour at 160-200°.



Semicarbazides and Carbazides.

Semicarbazide base[73] decomposes on standing into hydrazodicarbonamide. Once prepared, therefore, it should be utilized immediately.

Phenyl semicarbazide[74] suffers decomposition at 160-170° into phenylurazole and diphenyl-urazine. These substances, together with some unchanged phenylsemicarbazide comprise the residue. Ammonia, carbon dioxide, nitrogen and benzene pass out as vapors. Carbon monoxide is definitely absent. The identification, by Poth and Bailey, of diphenyl-carbazide in the fused mass furnishes a clue regarding the reaction mechanism. It would seem that the first stage is a "dearrangement", such as has already been expounded with phenylurea, phenylthiourea and others. Thus:

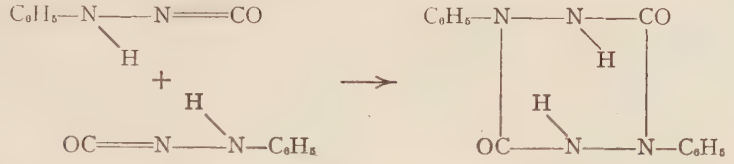
$$C_6H_5NH{-}NH{-}CO{-}NH_2 \rightleftharpoons \begin{cases} C_6H_5NH{-}NH_2 + HNCO \\ C_6H_5NH{-}N{=}C{=}O + NH_3 \end{cases}$$

Then the two compounds thus formed may combine to form diphenylcarbazide, $CO(NHNHC_6H_5)_2$:

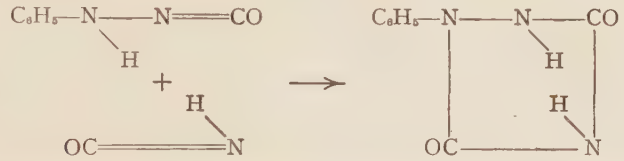
$$C_6H_5NH{-}NH_2 + C_6H_5NH{-}N{=}C{=}O \longrightarrow CO(NHNHC_6H_5)_2$$

[72] Grànacher and Gulbas, *Helv. Chim. Acta* **10**, 819 (1927).
[73] Thiele, *Ann.* **270**, 45 (1897); **271**, 127 (1892).
[74] Pinner, *Ber.* **21**, 1224 (1888); Poth and Bailey, *J. Am. Chem. Soc.* **45**, 3008 (1923).

or the second of the two compounds may react with itself to form diphenylurazine:



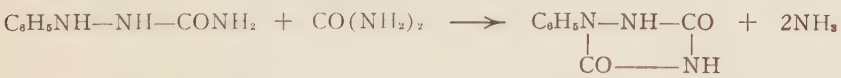
On the other hand, if the second compound accepts a molecule of *iso*-cyanic acid, phenyl urazole is the resulting product:



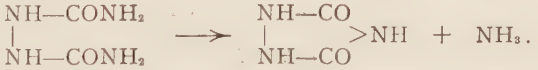
This reaction mechanism contains the essence of that suggested by Poth and Bailey, but it differs from it in detail. The details, however, emphasize the strict similarity in the pyrolytic behavior of semicarbazides and ureas. Poth and Bailey [75] postulated the following equations for the formation of phenylurazole:

$$2C_6H_5NH{-}NH{-}CONH_2 \rightleftharpoons (C_6H_5NH{-}NH)_2CO + CO(NH_2)_2$$

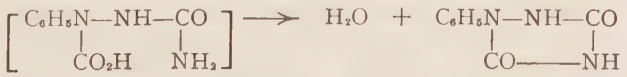
and then



Hydrazodicarboxamide [76] undergoes a slow transformation into urazole at 200°:



This bears a resemblance to the change from succinamide to succinimide. Phenyl semicarbazide-*N*-carboxylic acid [77] loses water spontaneously, changing thereby into phenylurazole:

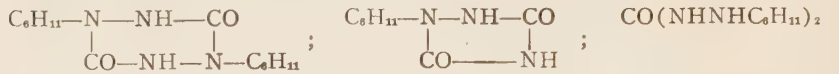


[75] Poth and Bailey, *loc. cit.*; Skinner and Ruhemann, *Ber.* **20**, 3373 (1887) showed that the first of these two reactions is reversible.

[76] Thiele and Stange, *Ann.* **283**, 41 (1894).

[77] Rupe and Gebhardt, *Ber.* **32**, 12 (1899); Wheeler and Beardsley, *Am. Chem. J.* **27**, 270 (1902).

Cyclohexyl-semicarbazide[78] behaves very much like phenylsemicarbazide in its course of reaction. Its pyrolysis (180-185° for 90 minutes) leads to a 34 percent yield of dicyclohexyl-urazine; a 13.8 percent yield of cyclohexyl-urazole; small amounts of dicyclohexylcarbazide; and a considerable quantity of ammonia.

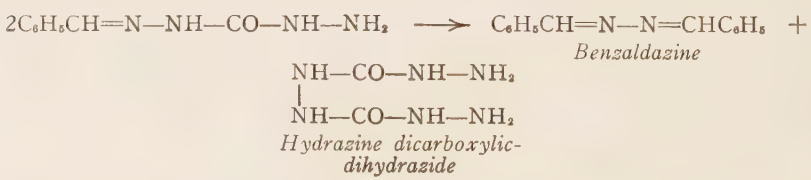


Dicyclohexyl urazine *Cyclohexylurazole* *Dicyclohexylcarbazide*

A 40 percent yield of the carbazide is obtainable if the semicarbazide is heated to 200° for a shorter period of time (12 minutes). In this experiment, there is no urazole, nor urazine, and about one-fifth of the original semicarbazide escapes decomposition. The most satisfactory way to prepare dicyclohexylcarbazide from the corresponding semicarbazide is to heat the latter in urethane as a solvent (150-160° for 15 min.). The yield is 73 percent.

If cyclohexyl semicarbazide hydrochloride is used instead of the free base, more than double the yield of dicyclohexyl-urazine is obtained (30 minutes at 200-210°). The mechanism for all of these changes is analogous to that presented on page 623.

The pyrolysis of semicarbazones or carbazones of aldehydes and ketones has been studied only in a few cases. Their mode of decomposition is not as involved as their rather complex structure would lead one to infer. Benzaldehyde-δ-aminosemicarbazone[79] is unchanged in boiling alcoholic solution, but is altered in hot toluene solution in accordance with the equation:



Benzaldazine *Hydrazine dicarboxylic-dihydrazide*

Hydrazine dicarboxylic-dihydrazide is further decomposed into 4-amino-urazole, $\begin{matrix}NH{-}CO\\ |\quad\quad >N{-}NH_2\\ NH{-}CO\end{matrix}$, and hydrazine if the pyrolysis is performed above 173°, the melting point of the original amino-semicarbazone.

Dibenzaldehyde carbohydrazone forms benzaldazine by boiling in absolute alcohol, as it does also if it is heated at 205° for an hour. In the latter case, however, 4-amino-urazole is also synthesized, which is

[78] Poth and Bailey, *J. Am. Chem. Soc.* **45**, 3010 (1923).
[79] Brown, Pickering and Wilson, *J. Chem. Soc.* **1927**, 107.

not the case in the former. Equations picture these transformations as follows:

$$CO(NH{-}N{=}CHC_6H_5)_2 \xrightarrow{\text{hot alcohol}} (C_6H_5CH{=}N{-})_2 + (\text{—NH—CO—NH—N=CHC}_6H_5)_2$$

$$CO(NH{-}N{=}CHC_6H_5)_2 \xrightarrow{205^\circ} (C_6H_5CH{=}N{-})_2 + (C_6H_5{-}CH{-}N{-})_2 + \begin{matrix} NH{-}CO \\ | \quad >N{-}NH_2 \\ NH{-}CO \end{matrix}$$

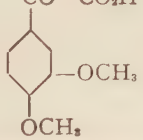
Diacetophenone carbohydrazone, $CO\left(\begin{matrix} NH{-}N{=}C{-}C_6H_5 \\ | \\ CH_3 \end{matrix}\right)_2$, undergoes pyrolysis in a strictly analogous fashion.

Benzaldazine is formed by decarboxylation[80] of the dicarboxy derivative of it (synthesized from phenylglyoxylic acid), at 180-200° (1 hour):

$$\begin{matrix} C_6H_5{-}C{=}N{-}N{=}C{-}C_6H_5 \\ | \qquad\qquad | \\ CO_2H \qquad CO_2H \end{matrix} \longrightarrow (C_6H_5{-}CH{=}N{-})_2 + 2CO_2.$$

If this aldazine is distilled at ordinary pressure, stilbene is formed in good yields:

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5 \longrightarrow N_2 + C_6H_5CH{=}CHC_6H_5.$$

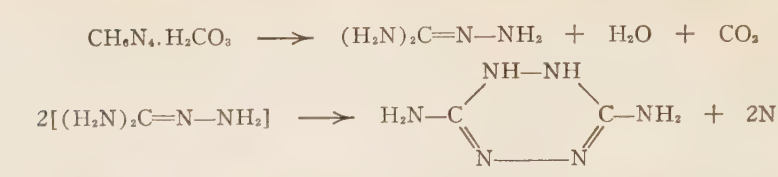
The anils of α-keto acids, $\begin{matrix} R{-}C{=}N{-}C_6H_5 \\ | \\ CO_2H \end{matrix}$, change by pyrolytic means[81] into Schiff's bases, $R{-}CH{=}NC_6H_5$. Since these may be hydrolyzed into aldehydes, it forms a method of synthesis for them which is sometimes convenient. With the glyoxylic acid related to veratrol,  , the aldehyde is formed in high yields.

Formyl thiosemicarbazide becomes dehydrated[82] at about 190° with the formation of a triazole-thiol:

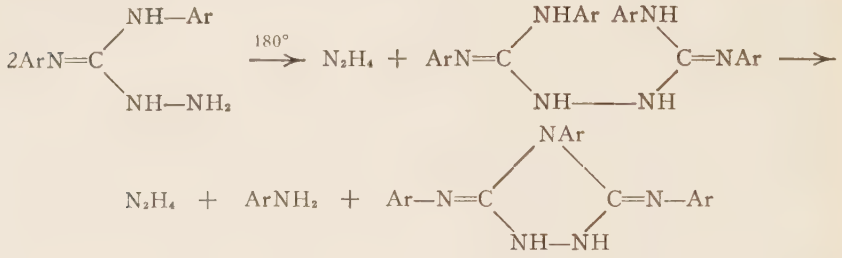
$$H{-}CO{-}NHNH{-}C(SH){=}NH \longrightarrow H_2O + \begin{matrix} N{-}NH \\ \| \quad \diagdown \\ \| \qquad C{-}SH \\ \diagup \quad \| \\ CH{-}N \end{matrix}.$$

The initial effect of heat[83] upon amino-guanidine bicarbonate is to liberate the free base, which then decomposes spontaneously into 3,6-diamino-1,2,4,5-tetrazine-dihydride:

[80] Bouveault, *Bull. soc. chim.* [3] **15**, 1019 (1896).
[81] Bouveault, *loc. cit.* p. 1020; *Compt. rend.* **122**, 1543 (1896).
[82] Freund and Meinecke, *Ber.* **29**, 2484 (1896).
[83] Ponzio and Gastaldi, *Gazz. chim. ital.* **45**, I, 181 (1915).



The triaryl guanazoles are formed when *N,N'*-diaryl-*N''*-amino-guanidines are heated.[84] This is quite general with varying types of aryl radicals. To illustrate:

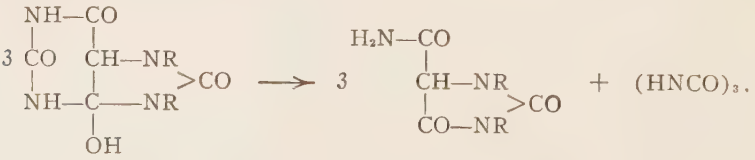


Triaryl-guanazole

The triphenyl- and the tri-*p*-tolyl-guanazoles have been prepared in this manner.

Urea, hydrogen cyanide, cyanuric acid and carbon are formed during the dry distillation of uric acid.[85] Alloxan gradually (during one year) decomposes[86] in a closed bottle, causing an accumulation of pressure due to carbon dioxide. The solid products of the decomposition are urea, oxalic acid and alloxantin.

Cyanuric acid is formed in almost quantitative yields as 7,9-dimethyl- (or diethyl)-4-hydroxy-4,5-dihydrouric acid changes into 1,3-dimethyl (or diethyl) hydantoyl amide; the conditions[87] are 30 minutes' heating at 230-250°:



[84] Busch and Ulmer *Ber.* **35**, 1720 (1902).
[85] Wöhler, *Pogg. Ann.* **15**, 626 (1829); Wöhler, *Ann.* **26**, 243 (1838).
[86] Gortner, *J. Am. Chem. Soc.* **33**, 85 (1911).
[87] Biltz and Lemberg, *Ann.* **432**, 143, 162, 169 (1923)

CHAPTER 21.

HYDRAZINES AND RELATED SUBSTANCES.

The substances with which this chapter is to deal will include compounds containing at least a chain of two nitrogen atoms, exclusive of the hydrazides which have been taken up with the amides, the semicarbazides which have been mentioned in the previous chapter, and the acid-azides which will be treated in a later chapter. Other azides will be given in this chapter.

Hydrazines

The initial effect of heat on *hydrazine dihydrochloride* is to expel one molecule of hydrogen chloride. At 200°, a more profound change [1] of simultaneous oxidation and reduction takes place:

$$3ClH_3N—NH_3Cl \longrightarrow 2HCl + N_2 + 4NH_4Cl.$$

Hydrazine dinitrate [2] melts at 103-104° by rapid heating, but it gradually decomposes at 85° into the volatile products; ammonia, nitric acid, nitrogen and water, and not into non-volatile hydrazine mononitrate and ammonium nitrate. The mononitrate is not completely decomposed even at 300°.

Hydrazine mono- and di-perchlorates behave rather similarly when heated. There is gradual initial decomposition as evidenced by slow gas evolution, but further heating causes an explosion. Hydronitric acid, chlorine, nitrogen and oxygen result, as well as chloride and hydroxide ions. The mono- and di-sulfates of hydrazine,[3] under similar conditions, fail to give hydronitric acid, but evolve hydrogen sulfide, sulfur dioxide and sulfur. Hydrazine monosulfate starts to decompose at 120°, but this is not rapid enough to produce frothing till 160°.

The thermal decomposition of hydrazine [4] is apparently mainly trimolecular:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2.$$

There is also a slight decomposition to yield hydrogen as well as ammonia and nitrogen, but it is interesting to note that this becomes

[1] Hofmann and Kroll, *Ber.* **57**, 937 (1924).
[2] Sabanejeff, *Z. anorg Chem.* **20**, 21 (1899).
[3] Turrentine, *J. Am. Chem. Soc.* **37**, 1111 (1915).
[4] Elgin, Askey and Taylor, St. Louis meeting of the American Chemical Society, April, 1928.

the main reaction with a photosensitized decomposition by excited mercury.

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2.$$

Ammonia is decomposed as fast as formed. The photochemical decomposition of hydrazine is similar to the latter, but is much slower. Any elucidation of the mechanism of these two decompositions is as yet merely speculative.

Phenylhydrazine boils at 241° with some decomposition. With four hours' heating [5] at 300°, the decomposition follows the equation:

$$2C_6H_5NHNH_2 \longrightarrow C_6H_6 + C_6H_5NH_2 + NH_3 + N_2.$$

If phenylhydrazine is heated [6] in the presence of its salt, aniline, but not benzene, is formed up to 140°; both aniline and benzene are formed at 160-175°:

$$2C_6H_5NH{-}NH_2 + C_6H_5NH{-}NH_3Cl \xrightarrow{140^\circ} 3C_6H_5NH_2 + N_2 + NH_4Cl$$

$$C_6H_5NH{-}NH_2 + C_6H_5NH{-}NH_3Cl \xrightarrow{175^\circ} C_6H_5NH_2 + C_6H_6 + N_2 + NH_4Cl$$

Hydrazobenzene, when heated in high-boiling solvents or when distilled, undergoes a transformation [7] into azobenzene and aniline. Other hydrazo compounds behave analogously. Thus, *p,p'*-hydrazotoluene pyrolyzes [8] into azotoluene and *p*-toluidine. In general:

$$2Ar{-}NH{-}NH{-}Ar \longrightarrow Ar{-}N{=}N{-}Ar + 2ArNH_2.$$

This reaction emphasizes the far greater stability of the azo- than the hydrazo-group.

The mechanism of this decomposition has received careful study, and two satisfactory proposals, somewhat akin to each other, are on record. Stieglitz [9] postulates the discharge of two electrons from the nitrogen of one molecule, producing azobenzene, and consequently releasing two positively charged hydrogen atoms; the nitrogen of a second molecule then absorbs the two liberated electrons, and this absorption causes scission of the nitrogen-to-nitrogen union in this second molecule thereby giving the two negative radicals, $C_6H_5NH{-}$, the power to absorb the two positively charged hydrogen atoms. The first slow decomposition reaction would thus be followed by an exceedingly rapid reduction reaction.

Wieland [10] assumes the elimination of two hydrogen atoms (rather than two electrons) from one molecule of hydrazobenzene, with the

[5] Walther, *J. prakt. Chem.* [2] **53**, 471 (1896).
[6] Busch and Knoll, *ibid.* **116**, 39 (1927).
[7] Melms, *Ber.* **3**, 554 (1870); Lermontow, *Ber.* **5**, 235 (1872); Stern, *Ber.* **17**, 380 (1884).
[8] Melms, *Ber.* **3**, 549 (1870).
[9] Stieglitz and Graham, *J. Am. Chem. Soc.* **38**, 1744 (1916).
[10] Wieland, *Ber.* **48**, 1098 (1915).

formation of azobenzene. Immediately thereafter, the nascent hydrogen reduces a second molecule of hydrazobenzene to aniline. Thus a slow reaction:

$$C_6H_5—NH—NH—C_6H_5 \longrightarrow C_6H_5—N=N—C_6H_5 + 2H,$$

is followed by a very rapid one:

$$C_6H_5—NH—NH—C_6H_5 + 2H \longrightarrow 2C_6H_5NH_2.$$

The fact that only one azo compound, and not three, results from mixed hydrazo compounds, R—NH—NH—R′, is good evidence for these theories, as is also the fact [11] that almost quantitative yields of azobenzene and triphenylmethane are formed when a mixture of hydrazobenzene and triphenylmethyl are refluxed in toluene for 5 hours. In this case, triphenylmethyl is the "hydrogen acceptor".

$$C_6H_5NH—NH—C_6H_5 \longrightarrow C_6H_5—N=N—C_6H_5 + 2H$$
$$2(C_6H_5)_3C + 2H \longrightarrow 2(C_6H_5)_3CH.$$

The mixed hydrazobenzenes which were investigated by Wieland include the following: p-$CH_3C_6H_4$—NH—NH—C_6H_5, p-$CH_3C_6H_4$—NH—NH—C_6H_4—OCH_3(p), p-$CH_3C_6H_4$—NH—NH—C_6H_4—Cl(p), C_6H_5—NH—NH—C_6H_4—$CO_2C_2H_5$(p), all of which pyrolyze at 125-170° in a solvent such as alcohol or xylene into the mixed azo compounds, and into equivalent amounts of the two amines. Small amounts of a semidine also appear. Stieglitz and Graham also obtained similar results with p-methyl-hydrazobenzene, $CH_3C_6H_4$—NH—NH—C_6H_5; p-bromo-hydrazobenzene; and dichloro-hydrazobenzene, (2,4)-$Cl_2C_6H_3$—NH—NH—C_6H_5. No hydrogen as such is formed in these experiments.

2-(β-Benzoylvinyl)-1-phenyl-hydrazine [12] behaves differently, the difference no doubt being due to the presence of a carbonyl group. At 185-187° and 14 mm. it changes into 1,5-diphenylpyrazole by loss of water:

$$C_6H_5CO—CH=CH—NH—NH—C_6H_5 \longrightarrow H_2O + \begin{matrix} CH—CH=C—C_6H_5 \\ \| \qquad\qquad | \\ N- \text{———} N—C_6H_5 \end{matrix}$$

A related reaction is encountered in compounds wherein the carbonyl group has been converted into a phenylhydrazone, as the change from the *bis*-p-nitrophenylhydrazine derivative of hydroxymethylene-acetophenone into 1-p-nitrophenyl-3-phenyl-pyrazole by long heating on the water bath shows:

[11] Goldschmidt and Wurzschmitt, *Ber.* **55**, 3216 (1922).
[12] von Auwers and Mauss, *Ann.* **452**, 207 (1927).

$$C_6H_5—C(=N—NH—C_6H_4NO_2)—CH=CH—NH—NH—C_6H_4NO_2 \longrightarrow$$

$$O_2N—C_6H_4—NHNH_2 \; + \; C_6H_5—C(=N—)—CH=CH—N=—C_6H_4NO_2$$

Phenacyl hydrazine,[12a] $C_6H_5COCH_2NHNH_2$, is fairly stable at 0°, but at 50° ammonia is liberated thereby leaving a dark brown mass.

Symmetrical *bis*-triphenylmethyl-hydrazine pyrolyzes at its melting point (220°) quantitatively into triphenylmethane and nitrogen:

$$(C_6H_5)_3C—NH—NH—C(C_6H_5)_3 \longrightarrow N_2 \; + \; 2(C_6H_5)_3CH.$$

It is of interest in this connection to note [13] that with zinc chloride as a catalyst, the reaction proceeds quite differently; the products of the reaction are well explained by assuming an initial scission between the nitrogens, followed by pyrolysis of one of the products (triphenylmethylamine) and rearrangement of the other (see p. 296):

$$(C_6H_5)_3C—NH—NH—C(C_6H_5)_3 \xrightarrow{ZnCl_2} [(C_6H_5)_3C—NH_2] \; + \; [(C_6H_5)_3C—N=]$$

$$[(C_6H_5)_3C—NH_2] \xrightarrow{\text{pyrolysis}} NH_3 \; + \; \underbrace{(C_6H_5)_3CH \; + \; (C_6H_4)_2CH—C_6H_5}_{\text{(Observed compounds)}}$$

$$[(C_6H_5)_3C—N=] \xrightarrow{\text{rearranges}} (C_6H_5)_2C=N—C_6H_5$$

It may not be amiss to point out the similarity between di-imide and azotriphenylmethane:[14] $[HN=NH]$ and $[(C_6H_5)_3C—N=N—C(C_6H_5)_3]$. Neither substance has ever been isolated, but instead each gives nitrogen. Triphenylmethyl appears in the latter case, and hydrazine in the former, the cause of the hydrazine production evidently being traceable to the vigorous reducing action of atomic hydrogen.[15] This instability of the azo grouping in these cases is undoubtedly occasioned by the great desire for the two nitrogen atoms to assume the stable structure of the nitrogen molecule, and it is not prevented from so doing by such a mobile atom as hydrogen, or by such a loosely bound group as triphenylmethyl. If azotriphenylmethane is the intermediate product in the pyrolysis of the hydrazo compound, one should expect only an ephemeral existence for it. The two triphenylmethyl molecules thus liberated would become hydrogen acceptors for the nascent hydrogen. However, this mechanism should permit the formation of some triphenylmethyl-amine, but this was not noticed. If, instead, triphenylmethyl is first liberated:

$$(C_6H_5)_3C—NH—NH—C(C_6H_5)_3 \longrightarrow 2[(C_6H_5)_3C] \; + \; [H—N=N—H],$$

[12a] Busch, Foerst and Stengel, *J. prakt. Chem.* **119**, 287 (1928).
[13] Stieglitz and Brown, *J. Am. Chem. Soc.* **44**, 1277, 1284 (1922).
[14] Wieland, *Ber.* **42**, 3020 (1909).
[15] *See* Thiele, *Ann.* **271**, 130 (1892).

the mechanism for the eventual production of triphenylmethane remains the same, but in this case there would seem to be the advantage that it explains the non-formation of ammonia or of triphenylmethylamine, $(C_6H_5)_3C—NH_2$, since hydrogen atoms appear *after* the formation of the triphenylmethyl.

When triphenyl-hydrazine is heated in boiling xylene [16] under an atmosphere of carbon dioxide, it undergoes pyrolysis with the formation of diphenylamine, aniline, azobenzene and quinone-anil-diphenyl-hydrazone, $C_6H_5N{=}C_6H_4{=}N—N(C_6H_5)_2$. For an explanation of this transformation it is better to assume an initial dissociation into diphenylamine and phenyl-imide:

$$(C_6H_5)_2N—NH—C_6H_5 \longrightarrow (C_6H_5)_2NH + [C_6H_5—N{=}],$$

than to assume the production of two free radicals by a simple scission of the N—N bond. Phenyl-di-*p*-tolyl-hydrazine, $(CH_3C_6H_4)_2N—NHC_6H_5$, changes quite analogously into azobenzene, aniline, di-*p*-tolylamine and quinone-anil-di-*p*-tolylhydrazone. The latter compound, of course, is regarded as coming from the interaction of phenyl-imide with the original triarylhydrazine.

Tetrabenzyl-hydrazine distils [17] at a temperature of 260° and 32 mm. pressure with partial decomposition into dibenzylamine and benzal-benzylamine; thus, in part,

$$(C_6H_5CH_2)_2N—N(CH_2C_6H_5)_2 \longrightarrow (C_6H_5CH_2)_2NH + C_6H_5CH_2—N{=}CH—C_6H_5$$

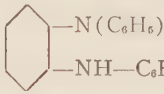
Tetraphenyl-hydrazine has an important point in common with hexaphenylethane, since both dissociate readily [18] into free radicals. Diphenylnitrogen makes its appearance at 90°:

$$(C_6H_5)_2N—N(C_6H_5)_2 \longrightarrow 2(C_6H_5)_2N.$$

In boiling toluene solution, this radical is formed momentarily, and then changes into diphenyldihydrophenazine and diphenylamine, by simultaneous oxidation and reduction (see p. 20):

$$4(C_6H_5)_2N \longrightarrow 2(C_6H_5)_2NH + C_6H_4\begin{smallmatrix}\diagup\ \diagdown\\ \diagdown\ \diagup\end{smallmatrix}C_6H_4,$$

(the two bridging nitrogens of the dihydrophenazine each carry a C_6H_5 group)

and into *o*-anilinotriphenylamine,  , by polymerization.

Other tetraarylhydrazines have also been found to dissociate in this

[16] Wieland and Reverey, *Ber.* **48**, 1112 (1915).
[17] Wieland and Schamberg, *Ber.* **53**, 1334 (1920).
[18] Wieland and others, *Ann.* **381**, 200 (1911); **392**, 127 (1912); *also*, Wieland, "Die Hydrazine," Stuttgart, F. Enke 1913, p. 73.

manner. Furthermore, mixed dialkyl-diaryl-hydrazines [19] have also been shown to dissociate into bivalent nitrogen radicals. With dimethyl-diphenyl-hydrazine this is noticeable by ordinary distillation, since appreciable quantities of methyl aniline are in the distillate and a red residue of polymerized "methylene aniline" remains in the flask:

$$C_6H_5N(CH_3)\text{—}N(CH_3)\text{—}C_6H_5 \longrightarrow 2\left(C_6H_5\text{—}N(CH_3)\right) \longrightarrow (C_6H_5\text{—}N{=}CH_2)_x + C_6H_5NHCH_3.$$

Furthermore, if nitric oxide is passed for an hour into a hot xylene solution of the hydrazine, there is formed methyl phenyl nitrosamine.

The unsymmetrical dialkyl-diaryl-hydrazines are much more stable than the symmetrical ones. As evidence of this, *N,N*-diethyl-*N'*,*N'*-diphenyl-hydrazine is not appreciably changed [20] after hours of refluxing in xylene solution.

Azo Compounds.

Aliphatic Azo Compounds.

Thiele [21] observed that azomethane, if diluted by carbon dioxide to avoid explosions, decomposes into nitrogen, ethane, methane and ethylene. This may be taken as evidence that the pyrolysis proceeds as follows:

$$CH_3\text{—}N{=}N\text{—}CH_3 \longrightarrow N_2 + 2[CH_3],$$

and immediately,

$$2[CH_3] \swarrow\!\searrow \begin{matrix} CH_3\text{—}CH_3 \\ CH_4 + \tfrac{1}{2}C_2H_4. \end{matrix}$$

It is rather significant that the scission does not take place between the nitrogen atoms. Although the double bond is frequently regarded as a "position of weakness" in the molecule, it never appears to be so in pyrolytic processes. This has been apparent in the discussion of olefine hydrocarbons, and it will be shown that the doubly-bound nitrogen-to-nitrogen linkage is never broken by thermal means.

This principle is the more readily visualized in the case of azomethane if the formula is written in accordance with the present day concept of electrons. Six electrons are shared between the two nitrogen atoms, $H:\ddot{C}(H):N:::N:\ddot{C}(H):H$. In elemental nitrogen, six electrons are similarly shared, $:N:::N:$. Therefore, with the structure of the nitro-

[19] Wieland and Fressel, *Ann.* **392**, 148 (1912).
[20] Wieland and Schamberg, *Ber.* **53**, 1329 (1920).
[21] Thiele, *Ber.* **42**, 2575 (1909).

gens in azo-methane so very similar to that of free nitrogen, the two methyl groups must be very loosely attached. In fact, in the case of azo-triphenylmethane it has been related how the triphenylmethyl groups cannot be made to remain attached. At the time of decomposition of azomethane, the following radicals must be present,

(*A*) (*B*)

Radical (*A*) can become satisfied in one of two ways; either it can unite with radical (*B*), or it may capture a hydrogen from radical (*B*) to form ethane or methane respectively. In the latter case, a methylene residue, [H:C:H], would remain from (*B*), which would polymerize to ethylene.

The decomposition of azomethane [22] between 280-330° is homogeneous at all pressures from 0.0259 cm. to 70.79 cm. It is strictly unimolecular only at the higher pressures, and is unimolecular to lower pressures if the temperature is low. The velocity constant at the lowest pressure is reduced to less than one-fourth of its high-pressure value when the temperature is 290°, and to one-tenth of the high-pressure value at 330°. Lewis [23] believes that collisions are adequate to account for the activation of the unimolecular decomposition of azomethane. Calculations reveal that collisions may account for the activation of 1.07×10^{20} mols per cc. per second, and Ramsperger observed that the rate of decomposition was 1.67×10^{15} mols per cc. per second.

Azo-*iso*propane [24] has been studied between 250-290°, at initial pressures from 4.60 cm. to 0.025 cm. It is a homogeneous, unimolecular reaction throughout. Apparently, 85 percent of the reaction follows the equation:

$$C_3H_7—N=N—C_3H_7 \longrightarrow N_2 + C_6H_{14},$$

and 15 percent according to an alternative equation:

$$C_3H_7—N=N—C_3H_7 \longrightarrow N_2 + C_3H_6 + C_3H_8.$$

Symmetrical diphenylazomethane,[25] $C_6H_5CH_2—N=N—CH_2C_6H_5$, decomposes analogously in a vacuum at a temperature of 175-180°, giving dibenzyl. The oxidation product of diphenyl-hydrazoethane (symmetrical di-methylphenylmethyl-hydrazine) presumably is an azo

[22] Ramsperger, *J. Am. Chem. Soc.* **49**, 912, 1495 (1927).
[23] B. Lewis, *Proc. Natl. Acad. Sci.* **13**, 546 (1927); *Chem. Abstracts* **21**, 3526 (1927).
[24] Ramsperger, *J. Am. Chem. Soc.* **50**, 714 (1928); *Proc. Natl. Acad. Sci.* **13**, 849 (1927).
[25] Thiele, *Ann.* **376**, 239 (1910).

compound with the structure: $CH_3-CH(C_6H_5)-N=N-CH(C_6H_5)-CH_3$. When this is heated [26] in a vacuum, nitrogen is evolved and 2,3-diphenylbutane, boiling point (40 mm.) 205-215°, distils over. The following reaction [27] occurs quantitatively at 90-100°:

$$(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2 \longrightarrow N_2 + (CH_3)_2C(CN)-C(CN)(CH_3)_2.$$

Ethyl hyponitrite differs from azo compounds in that the two nitrogens are attached to oxygen atoms instead of carbons. It decomposes [28] by heating, even in warm water, into alcohol, aldehyde and nitrogen:

$$C_2H_5-O-N=N-O-CH_2-CH_3 \longrightarrow N_2 + C_2H_5OH + O=CH-CH_3.$$

Benzyl hyponitrite, $C_6H_5CH_2ON=NOCH_2C_6H_5$, accordingly changes into benzyl alcohol and benzaldehyde.

The yellow needles of potassium salt of azo-dicarboxylic acid [29] decompose above 100° and leave a residue of potassium carbonate:

$$KO_2C-N=N-CO_2K \longrightarrow N_2 + CO + K_2CO_3.$$

Azodicarboxthioamide dimethyl ester behaves in a rather complex manner. At 110°, it decomposes explosively [30] into the corresponding hydrazo compound:

while simultaneously nitrogen, cyanogen, methyl thiocyanate, dimethyl sulfide, a little iminothiourazole methyl ether, and traces of ammonia and methyl mercaptan are formed.

Dimethyl azodi-thiolcarboxylate breaks down at 80-105° according to two mechanisms, both apparently in equal amounts since the liberated volumes of nitrogen and of carbon monoxide are about equal:

$$CH_3S-CO-N=N-CO-SCH_3 \begin{cases} \longrightarrow N_2 + 2CO + (CH_3)_2S_2 \\ \longrightarrow N_2 + (COSCH_3)_2 \end{cases}$$

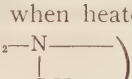
Tetrazenes, with the nucleus $=N-N=N-N=$, undergo pyrolyses which are quite comparable to those of aliphatic azo compounds. Tetraethyltetrazene, $(C_2H_5)_2N-N=N-N(C_2H_5)_2$, decomposes gradually

[26] Schulze and Lochte, *J. Am. Chem. Soc.* **48**, 1034 (1926).
[27] Thiele and Hauser, *Ann.* **290**, 5, 30 (1896).
[28] Zorn, *Ber.* 11, 1630 (1878).
[29] Thiele, *Ann.* **271**, 130 (1892).
[30] Arndt, Milde and Eckert, *Ber.* **56**, 1976 (1923).

when it is refluxed at atmospheric pressure (about 140°). About 80 percent of it is thereby transformed into nitrogen, diethylamine and ethyl ethylideneamine, $CH_3—CH=N—C_2H_5$, if precautions are taken to permit the escape of the latter as it is formed. Otherwise, its low boiling point (60-70°) inhibits further decomposition. The formation[31] of $(C_2H_5)_2N$ groups may be demonstrated by passing a slow current of nitric oxide over the decomposing tetrazene, whereby nitrosodiethylamine is produced. Tetrabenzyltetrazene changes into dibenzylamine and benzyl-benzylidene amine, on heating for 6 hours in boiling xylene:

$$((C_6H_5CH_2)_2N—N=)_2 \longrightarrow N_2 + 2[(C_6H_5CH_2)_2N] \longrightarrow (C_6H_5CH_2)_2NH + C_6H_5CH=N—C_7H_7.$$

By a similar procedure, *N*-azopiperidine (dipiperyl-tetrazene), $(CH_2)_5=N—N=N—N=(CH_2)_5$, is converted into nitrogen, piperidine, and tetrahydropyridine, .

Dibenzyl-diphenyl-tetrazene gives rise to a rapid evolution[32] of nitrogen when heated in boiling xylene. The corresponding hydrazine,  , is formed. A like change for dimethyl-diphenyl-tetrazene and for diethyl-diphenyl-tetrazene was found by Wieland and Fressel, thereby discrediting the earlier report of Franzen and Zimmermann that ammonia and phenyl *iso*cyanide may be formed from dimethyl-diphenyl-tetrazene "in recht guter Ausbeute".

The azo-nitrogens of *β*-tetranaphthyl tetrazene,[33] $(C_{10}H_7)_2N—N=N—N(C_{10}H_7)_2$, are quickly detached in boiling toluene. The resinous mass which remains in the toluene solution represents polymerization products of dinaphthylnitrogen, $(C_{10}H_7)_2N$. The compound from carbazole, namely, dibiphenylene-tetrazene, $(C_6H_4)_2N—N=N—N(C_6H_4)_2$, is more stable than other tetrazenes, but it loses its azo nitrogen in hot xylene in the presence of a little copper-bronze.

Aromatic Azo Compounds.

Insofar as the azo part of aromatic azo compounds is concerned, aromatic azo compounds possess a far greater stability than their aliphatic analogs. Azobenzene, for example, may be distilled (boiling point 295°) without decomposition. Similarly, *p*-aminoazobenzene boils above 360° with little or no deterioration. If the vapors of azobenzene are passed through a glowing tube, they may decompose with sudden-

[31] Wieland and Fressel, *Ann.* **392**, 141 (1912).
[32] Franzen and Zimmermann, *Ber.* **39**, 2567 (1906).
[33] Wieland and Süsser, *Ann.* **392**, 182 (1912).

ness.[34] Ferko observed [35] only benzene and diphenyl as pyrolytic products. In addition, Claus [36] had previously reported anthracene and chrysene but Ferko could not confirm this result. As gases, Claus noticed nitrogen, hydrogen cyanide and ammonia.

A modification of this reaction [37] has been utilized by Gomberg in the preparation of tetraphenylmethane, although in only 2 percent yields. In this preparation, the mixed azo compound with phenyl and triphenylmethyl groups was merely melted:

$$C_6H_5—N{=}N—C(C_6H_5)_3 \longrightarrow N_2 + C_6H_5—C(C_6H_5)_3.$$

By employing solvents, Wieland [38] demonstrated that the evolution of nitrogen is quantitative at 80°, and that 35 percent of the triphenylmethyl radical remains in solution as such. One might suspect that this would force the phenyl radical to combine with itself, but this is not the case. Benzene is formed, but no diphenyl.

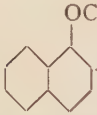
Similarly, in ligroin at 80°, $(C_6H_5)_3C—N{=}N—C_6H_4Cl(p)$ gives triphenylmethyl and chlorobenzene, and $(p\text{-}CH_3C_6H_5)_3C—N{=}N—C_6H_4Cl$ changes into tri-*p*-tolylmethyl and chlorobenzene on being heated dry at 116°. The *p*-nitrophenyl compound, $(C_6H_5)_3C—N{=}N—C_6H_4NO_2$, is quite stable, considering the presence of the nitro group. In fact, it was reported to be the most stable of the compounds studied. The great attraction of *p*-nitrophenyl for its valence electrons has previously been noticed in another connection (pp. 37, 39). At 90° in xylene, this substance yields triphenylmethyl and nitrobenzene (which was identified as aniline). Other similar compounds were also studied.

Compounds of the type, $(C_6H_5)_3C—N{=}N—CO—R$, lose nitrogen and form colored solutions, when they are heated in an inert atmosphere.[38a] In these experiments, R represents methyl or benzyl. Lorenzo ascribed the color to the radicals which were stable for a time, but ultimately combined to form the pinacolone, $(C_6H_5)_3C—CO—R$, whereupon the color vanishes.

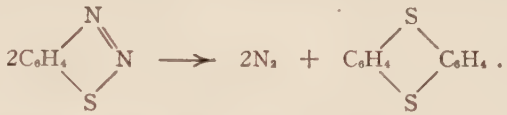
No accurate picture of the reaction mechanism for the formation of benzene, instead of diphenyl, in this type of pyrolysis can be made. It may be similar to the somewhat related fact that hydroxyl ions, set free at the anode, yield water and oxygen instead of hydrogen peroxide.

A little above the melting point (67°) of the nitrate of the mixed

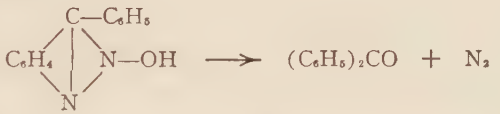
[34] Meyer and Hofmann, *Monatsh.* **38**, 343 (1917).
[35] Ferko, *Ber.* **20**, 660 (1887).
[36] Claus, *Ber.* **8**, 37 (1875).
[37] Gomberg, *Ber.* **36**, 1088 (1903).
[38] Wieland, Popper and Siegfried, *Ber.* **55**, 1816 (1922); *Rec. trav. chim.* **41**, 576 (1922)
[38a] Lorenzo, *Anales soc. españ. fis. quim.* **26**, 98 (1928).

azo compound,  , there is a pyrolysis [39] into α-nitro-β-methoxynaphthalene and benzenediazonium nitrate. If heated much above the melting point, the latter compound is destroyed. Various homologs of the original azo compound all behave similarly; thus, phenyl may be replaced by tolyl, xylyl, anisyl, phenetyl, etc., or methoxy by ethoxy.

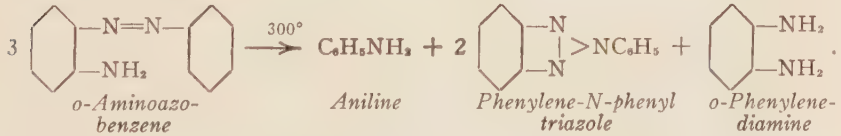
o-Phenylene diazosulfide [40] pyrolyzes into a thianthrene body at 200°:



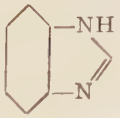
2-Hydroxy-3-phenylindazole also loses nitrogen by heating (above melting point 125°). This transformation proceeds especially well [41] by heating *in vacuo*.



The *o*-aminoazo compounds behave differently from the others which have been mentioned, and this is due mainly to the *o*-amino group. The following reaction [42] is typical:

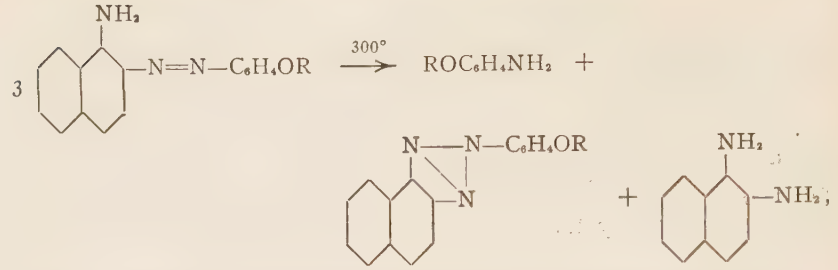


o-Aminoazobenzene — *Aniline* — *Phenylene-N-phenyl triazole* — *o-Phenylenediamine*

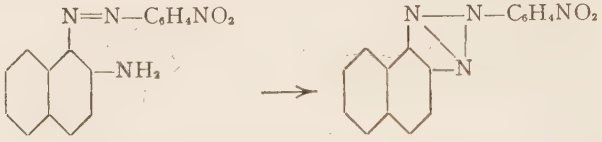
Some azimino-benzene,  , is also formed.

The formation of *N*-aryltriazoles by this method is quite a general reaction, and it has been applied not only in the benzene series but also in the naphthalene series,[43] as in the case of naphthylene-*N*-aryltriazoles:

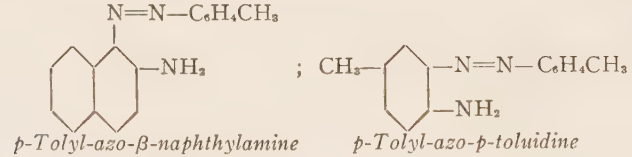
[39] Charrier and Ferreri, *Gazz. chim. ital.* **43**, II, 148, 211 (1913).
[40] Jacobson and Ney, *Ber.* **22**, 910 (1899); Jacobson and Janssen, *Ann.* **277**, 225 (1893).
[41] Auwers, *Ber.* **29**, 1266 (1896).
[42] Charrier and others, *Gazz. chim. ital.* **52**, I, 261 (1922).
[43] Ferreri, *Atti. accad. sci. Torino* **49**, 497; *Chem. Abstracts* **8**, 2686 (1914).



or in the quite analogous synthesis [42] of *N*-*p*-nitrophenyl-1,2-naphthotriazole:



or in the pyrolysis [44] of *p*-tolyl-azo-β-naphthylamine, or of *p*-tolyl-azo-*p*-toluidine:



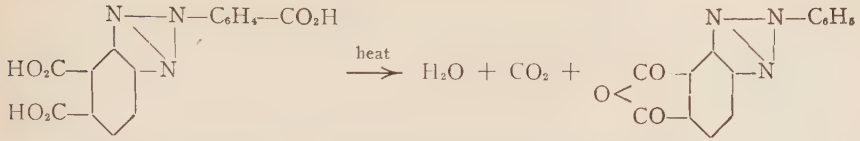
p-Tolyl-azo-β-naphthylamine *p-Tolyl-azo-p-toluidine*

Very interesting also is the fact that these triazoles may be made from the *o*-azido-azo bodies [45] by heat:

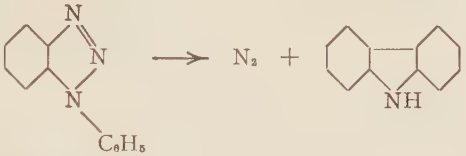
Crippa [46] has reported that the transformation of aryl-azo-aniline, Ar—N=N—C_6H_4—NH_2(*o*), into *N*-aryl-triazoles, *o*-diamines and aryl-amines takes place in 10 minutes at 280° (with oil of vaseline) in the presence of copper powder, whereas similar results in hot nitrobenzene occurred in ten hours, and in hot turpentine (boiling point 155°) in fifty hours.

The following pyrolysis of a substituted triazole [47] has nothing to do with *o*-aminoazo compounds, but is listed here because of its relationship to the triazoles:

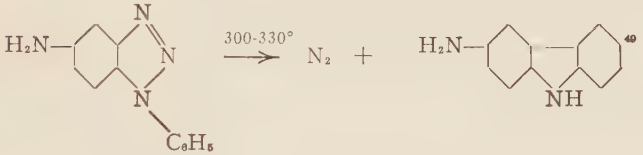
[44] Charrier, *Gazz.* **40**, II, 132 (1910).
[45] Zincke and Lawson, *Ber.* **19**, 1456 (1886).
[46] Crippa, *Gazz. chim. ital.* **55**, 706 (1925).
[47] Charrier and others, *Gazz. chim. ital.* **52**, I, 272 (1922).

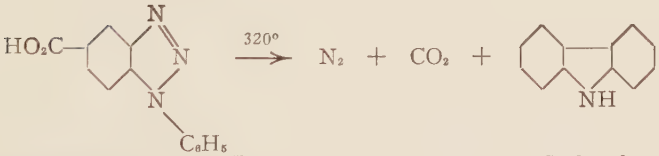


Above 300°, *N*-phenylaziminobenzene changes into carbazole and related compounds behave similarly. It distils at 360°.[48]



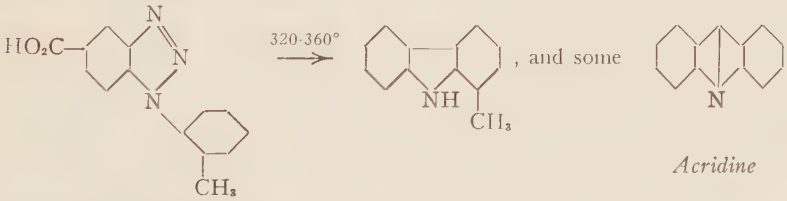
N-Phenylaziminobenzene *Carbazole*





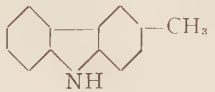
Phenaziminobenzoic acid[50] *Carbazole*

In the latter case, better yields are obtained if 3 to 4 parts of calcium carbonate are added. Similarly, at 320-360°, there is the reaction:



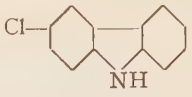
Acridine

The related *p*-tolyl compound gives an 84 percent yield of



when it is heated with lime to assist in the decarboxylation. Nearly a quantitative conversion (7 grams into 6 grams) of *N*-phenyl-*m*-chloro-

[48] Graebe and Ullmann, *Ann.* **291**, 16 (1896).
[49] Ullmann, *Ber.* **31**, 1697 (1898); *Ann.* **332**, 100 (1904).
[50] Ullmann, *Ann.* **332**, 84 (1904).

azimidobenzene into chlorocarbazole,  , results from boiling.

Usually, one is accustomed to regard azo dyes as being fast to ironing, but blue and violet benzidine dyes become corinth-red when the dyed cotton is touched with a hot iron.[51] This is probably a colloidal effect, however, rather than a pyrolytic one. It confirms the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the fiber blue and the smaller corinth-red. Thus, heat increases the degree of dispersion. Since the red color may also be formed, although more imperfectly, by desiccation over sulfuric acid, the color changes may thus be connected with dehydration and simultaneous increase in the degree of dispersion.

Diazoamino Compounds.

By diluting diazoaminobenzene[52] with sand, or better, with 8-10 volumes of paraffin oil, nitrogen is liberated at 150° and continues for two hours. Neither benzene nor aniline nor diphenylamine is produced, but in the paraffin oil is a small quantity of a mixture of *o*- and *p*-aminobiphenyl. From 100 grams of diazoaminobenzene, 4 grams of the sulfates of these bases was eventually isolated.

$$C_6H_5N{=}N{-}NH{-}C_6H_5 \longrightarrow N_2 + C_6H_5{-}C_6H_4NH_2.$$

Because of the great stability of *p*-aminoazobenzene, it is rather unreasonable to consider it as an intermediate product in this pyrolysis, although some types of acyl-anilides are known to rearrange by thermal means:

$$C_6H_5{-}NCl{-}COCH_3 \longrightarrow Cl{-}C_6H_4{-}NH{-}COCH_3.$$

In fact, *N*-chloro-aniline, C_6H_5NHCl, is known[52a] to yield *o*-chloro-aniline (18-16 percent yield), *p*-chloro-aniline (41-50 percent), 2,4-dichloro-aniline (4-6 percent), and aniline (3-6 percent) if it is heated at 100° in a sealed tube. Yokojima[52b] states that neither diazoaminobenzene nor its hydrochloride gives aminoazobenzene when heated alone. The presence of aniline is essential for this conversion.

By itself, diazoaminobenzene undergoes pyrolysis in two steps; one, at a bath temperature of 105-110° at which there is a gradual evolution of gas, and the second, which becomes explosive at 130-135°. This latter condition is reached after about two hours of heating, beginning

[51] Haller, *Kolloid-Z.* **38**, 248 (1926).
[52] Heusler, *Ann.* **260**, 227 (1890).
[52a] Bradfield, *J. Chem. Soc.* **1928**, 351.
[52b] Yokojima, *J. Soc. Chem. Ind.* (Japan) **31**, 100; **32B** (1928); *Chem. Abstracts* **22**, 2745 (1928).

at 105-110°. Just prior to the violent reaction, an oil commences to distil. The danger of explosion is entirely removed when paraffin oil is used as a solvent.

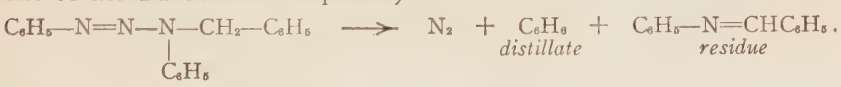
Benzene diazopiperidide,[53] in the absence of any solvent, starts to decompose at 225-230°, and appears to follow the equation:

$$C_6H_5{-}N{=}N{-}N(C_5H_{10}) \longrightarrow N_2 + C_6H_6 + C_5H_9N.$$

From 565 grams originally, 117.5 grams of residue, 353 grams of distillate, 83.7 grams of nitrogen are produced, and there is a loss of 10.8 grams. In the distillate are 52 percent of the calculated amount of benzene, and 10 percent of the possible amount of diphenyl. The substance C_5H_9N is a mixture of bases. Benzene diazodimethylamide, $C_6H_5N{=}N{-}N(CH_3)_2$, boils at 240° almost without decomposition, but by dropping it on hot sand it decomposes at 250°. Among the products of pyrolysis are benzene, diphenyl, dimethylamine and small quantities of another base.

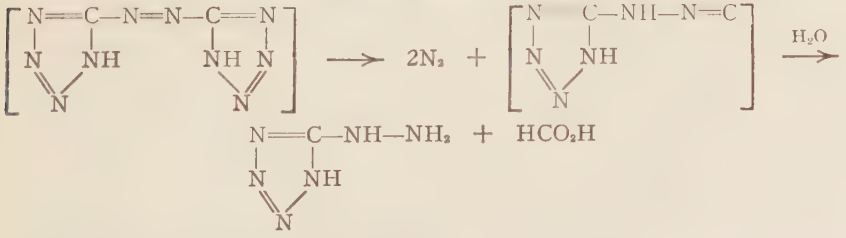
Diazoaminobenzene-*o*-carboxylic ester[54] becomes transformed into a ring compound, *N*-phenyl-*β*-phentriazone, by boiling in aqueous alcohol:

N-Benzyl-diazoaminobenzene[52] undergoes an interesting pyrolysis into nitrogen, benzene, and benzal-aniline by heating in paraffin (4 parts for one of the diazoamino compound):

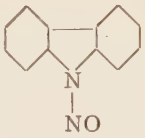
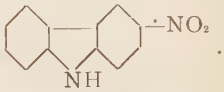


Other *N-N* Compounds.

The sodium salt of 5,5′-azotetrazole[55] is isolable, but by acidifying the solution, the azotetrazole decomposes spontaneously into tetrazolyl hydrazine and formic acid. Water plays a part in this reaction:



[53] Heusler, *ibid.* p. 227, 249.
[54] Mehner, *J. prakt. Chem.* [2] **63**, 266, 311 (1901).
[55] Thiele, *Ann.* **303**, 57 (1898).

In hot xylene, *N*-nitrosocarbazole,  , loses nitric oxide forming[56] much carbazole and little 2-nitrocarbazole,  .

Nitric oxide is also a product which results when diphenylnitrosamine, $(C_6H_5)_2N{-}NO$, is heated[57] in a vacuum above 40°.

Phenylnitramine, $C_6H_5{-}NH{-}NO_2$, undergoes pyrolysis[58] above 100° into nitrogen, carbon dioxide, nitrous acid, nitroaniline and nitrophenol. Benzene sulfo-nitroamide[59] evolves nitrous oxide stormily at 100°, and leaves a residue of benzenesulfonic acid:

$$C_6H_5SO_2{-}NH{-}NO_2 \longrightarrow N_2O + C_6H_5SO_3H.$$

Phenylhydrazones, Etc.

When the phenylhydrazone[60] of an aldehyde is heated, two main reactions occur, one leading to the formation of ethylene derivatives and the other to the production of Schiff's bases. The second of these reactions is by far the more prominent.

$$(1)\quad 2R{-}CH{=}N{-}NH\Phi \longrightarrow R{-}CH{=}CH{-}R + 2N_2 + 2\Phi H$$
$$(2)\quad 3R{-}CH{=}N{-}NH\Phi \longrightarrow 3R{-}CH{=}N\Phi + N_2 + NH_3.$$

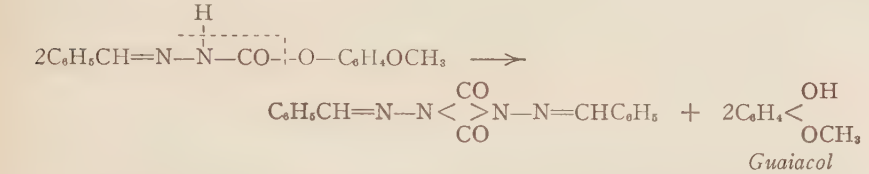
Thus, benzaldehyde phenylhydrazone, which melts at 156°, undergoes pyrolysis at 210° chiefly into benzylidine aniline, nitrogen and ammonia, and a far lesser amount of stilbene and benzene. Benzaldehyde *o*- and *p*-tolylhydrazones behave similarly, the pyrolysis occurring at 190°.

Phenylhydrazones of unsaturated ketones such as mesityl oxide are more prone by far to rearrange[61] into pyrazolines than are the phenylhydrazones of unsaturated aldehydes. The *p*-tolylhydrazone of benzalacetone undergoes a partial rearrangement by vacuum distillation:

The *p*-nitrophenylhydrazones are somewhat more stable. Refer to pages 39 and 636, for other instances of greater stability of *p*-nitrophenyl compounds.

[56] Wieland and Lecher, *Ann.* **392**, 168 (1912).
[57] Warquezrol and Florentin, *Bull. soc. chim.* **11**, 804 (1912).
[58] Bamberger and Landsteiner, *Ber.* **26**, 488 (1893); Bamberger, *Ber.* **27**, 2601 (1894).
[59] Hinsberg, *Ber.* **25**, 1092 (1892); **27**, 600 (1894).
[60] Chattaway, Cumming and Wilson, *J. Chem. Soc.* **99**, 1950 (1911).
[61] von Auwers and Kreuder, *Ber.* **58**, 1974 (1925).

The following equation refers to the pyrolysis of a rather complex hydrazone [62] of benzaldehyde (p. 618):



Guaiacol

The pyrolysis of benzaldehyde-δ-aminosemicarbazone, and related compounds, has been expounded on page 624. This type of compound is, of course, related to benzaldehydephenylhydrazone, although for obvious reasons the pyrolyses of the two types differ. Semicarbazide semicarbazones (from semicarbazide and the semicarbazones of hydroaromatic ketones) decompose [63] on heating into ammonia, tars, and (probably) hydrazine dicarboxamide, $H_2N{-}CO{-}NH{-}NH{-}CONH_2$.

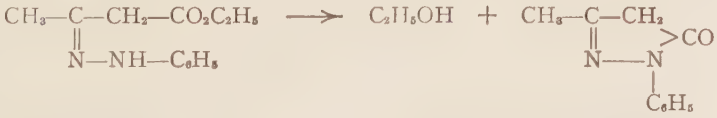
The malonyl-dihydrazone of ethyl acetoacetate,[64] $CH_2(CO{-}NH{-}N{=}C(CH_3){-}CH_2{-}CO_2C_2H_5)_2$, liberates ammonia when it is heated.

Hydrazones Which Form Cyclic Structures on Pyrolysis.

Some other reactive group than the hydrazone group must be present in the molecule for this type of behavior. Water, or aniline, or alcohol is usually eliminated, depending on the nature of these groups. Benzil osazone is pyrolyzed [65] to 2,4,5-triphenyl-1,2,3-triazole by distillation:

The yield is good in this case, although in most cases the yield of a triazole from osazones is very poor.

Pyrazolone formation [66] is noticed when the phenylhydrazone of ethyl acetoacetate is heated:

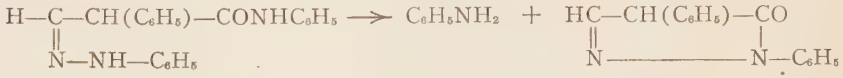


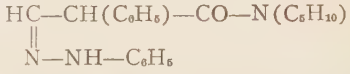
Phenylhydrazone of ethyl acetoacetate

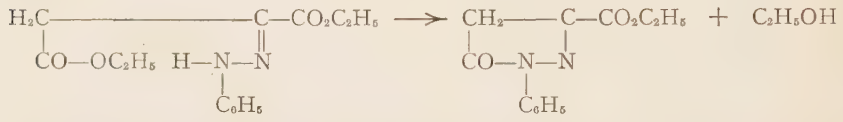
1-Phenyl-3-methyl-5-pyrazolone

[62] Diels and Grube, *Ber.* **53**, 854 (1920); *Ber.* **47**, 2185 (1914).
[63] Matzurevich, *J. Russ. Phys. Chem. Soc.* **56**, 19 (1925); *Chem. Abstracts* **19**, 3484 (1925).
[64] Bülow and Bozenhardt, *Ber.* **42**, 4784 (1909).
[65] Auwers and Meyer, *Ber.* **21**, 2806 (1888).
[66] Knorr, *Ann.* **238**, 147 (1887).

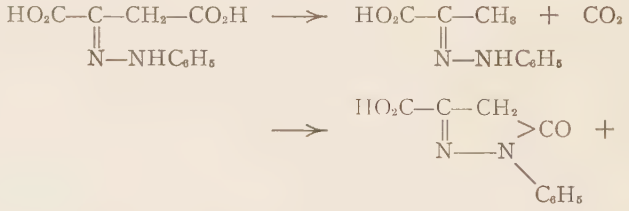
At 200-220°, the phenylhydrazone [67] of formyl-phenylacetanilide changes into 1,4-diphenyl-5-pyrazolone with the elimination of aniline:



The acetopiperidide analog,  , also gives the same pyrazolone as would be anticipated. Piperidine is liberated. Analogously, by heating the phenylhydrazone of ethyl oxaloacetate [68] on the water bath there is detachment of alcohol to produce a 5-membered ring:



Two reactions prevail at 100° with the phenylhydrazone of oxaloacetic acid. In one, carbon dioxide is eliminated in the manner of β-ketonic acids, whereas in the other, water is released [69] to effect a pyrazolone ring closure. Both reactions are unimolecular, but the latter differs in that it is catalytically accelerated by acids.



The preferential formation of a 5-membered over a 6-membered ring is apparent in the following reaction: [70]

Diethyl ester of 1-phenyl-5-pyrazolone-3-carboxyl-4-acetic acid

Six-membered rings are readily formed, however, when the 5-ring possibility is excluded. For example, with the phenylhydrazone of

[67] Wislicenus and Erbe, *Ann.* **421**, 119 (1920).
[68] Wislicenus, *Ann.* **246**, 321 (1888).
[69] Jones and Richardson, *J. Chem. Soc.* **81**, 1140 (1902).
[70] Wislicenus and Waldmüller, *Ber.* **44**, 1564 (1911).

α-ketoglutaric acid (p. 474), $\begin{matrix} HO_2C{-}C{=}N{-}NH{-}C_6H_5 \\ | \\ CH_2{-}CH_2{-}CO_2H \end{matrix}$, which becomes transformed into 1-phenyl-6-pyridazinone-3-carboxylic acid, or with the phenylhydrazone of levulinic acid [71] above 160° the following reaction occurs:

$$CH_3{-}\underset{\underset{N{-}NHC_6H_5}{\|}}{C}{-}CH_2{-}CH_2{-}CO{-}OH \xrightarrow{\text{above } 160^\circ} H_2O + CH_3{-}\underset{\underset{N{-}N{-}CO}{\|}}{C}{-}CH_2{-}CH_2$$
$$\qquad\qquad\qquad

Bouveault has developed a method by which aromatic α-keto acids may be converted either into aldehydes or into compounds related to stilbene. The principle of the method is to synthesize the hydrazone of the α-keto acid and then to decarboxylate the latter to an aldazine by heating at 180-200° for an hour:

$$2Ar{-}CO{-}CO_2H \longrightarrow \underset{\displaystyle CO_2H}{\overset{\displaystyle |}{Ar{-}C{=}N{-}N{=}C{-}Ar}}\underset{\displaystyle CO_2H}{\overset{\displaystyle |}{}} \longrightarrow (Ar{-}CH{=}N{-})_2.$$

By distillation at ordinary pressure, this aldazine changes into stilbene and nitrogen, or by hydrolysis it yields the aldehyde and hydrazine (see p. 625):

$$Ar{-}CH{=}N{-}N{=}CH{-}Ar \longrightarrow N_2 + ArCH{=}CHAr.$$

This has been applied with phenylglyoxylic acid, *p*-cresylglyoxylic acid and others.[75]

The fact that part of the nitrogen from *azines* is eliminated as ammonia is sufficient evidence[76] that the reaction is more complex than this simple mechanism infers. Benzalazine, $C_{14}H_{12}N_2$, undergoes pyrolysis at 275° into stilbene, and to a much lesser extent into a compound, $C_{28}H_{23}N_3$ (melting point 261° and boiling point 460°), of undetermined structure. With *p*-tolualazine, the unsaturated compound is still the chief product, but more ammonia appears. Di-*p*-amino-benzalazine gives much ammonia and tarry reaction products, and no compound related to stilbene since it is pyrolyzed at the temperature of the decomposition of the azine (307°). Nor could any of the stilbene be obtained from di-*p*-benzoxy-benzalazine, from piperonalazine, and traces only from β-methoxynaphthalazine.

Phenanthrene derivatives are formed from the azines which possess an unsubstituted *ortho* position. These *ortho* hydrogens are presumably the source of the hydrogen for the ammonia which is evolved. Aliphatic azines give no marked evolution of nitrogen or of ammonia. The yields of the stilbene derivatives, and the decomposition temperature of various azines are listed in the table on page 647.

Phosphazines.[77]

These compounds revert into their components by heating in a high vacuum:

$$R_2C{=}N{-}N{=}PR_2 \longrightarrow R_2C{=}N{\equiv}N + PR_3.$$

Of course, the resulting diazo compounds will lose nitrogen on continued

[75] Bouveault, *Bull. soc. chim.* [3] 15, 1019 (1896); *Compt. rend.* 122, 1491 (1895).
[76] Pascal and Normand, *Bull. soc. chim.* 9, 1029 (1911); 11, 21 (1912).
[77] Staudinger and Lüscher, *Helv. Chim. Acta* 5, 75 (1922).

TABLE LVIII. *Decomposition Temperatures of Various Azines and the Stilbene Derivatives Formed.*

Azine	Temperature °C.	Yield	Stilbene Derivative
Benzalazine	275	Good	Stilbene
p-Tolualazine	314	Good	Dimethyl stilbene
Cuminalazine	281	Good	Diisopropyl stilbene
p-Methyl-benzalazine	...	30-35 percent	$C_6H_5CH{=}CHC_6H_4CH_3$
Furfuralazine	...	15-20 percent	Furfurostilbene
Di-*p*-chlorobenzalazine	284	25 percent	Di-*p*-chlorostilbene
Di-*p*-aminobenzalazine	307	None (see above)	
Di-*p*-methoxybenzalazine	289	?	
Di-*o*-methoxybenzalazine	270	35 percent	Di-*o*-methoxystilbene
Di-*m*-methoxybenzalazine	...	30 percent	Di-*m*-methoxystilbene
Di-*o*-ethoxybenzalazine	287	30 percent	Di-*o*-ethoxystilbene
Di-*p*-ethoxybenzalazine	308	?	
Di-*o*-benzoxybenzalazine	...	Some	Di-*o*-benzoxystilbene
Di-*p*-benzoxybenzalazine	...	None	Di-*p*-benzoxystilbene

heating. In the case of $\begin{matrix} C_6H_5CO{-}C{=}N{-}N{=}P(C_6H_5)_3 \\ | \\ C_6H_5 \end{matrix}$, nitrogen is detached at the melting point, thereby yielding triphenyl phosphine and diphenyl ketene. Nitrogen is also eliminated from fluorenone triphenylphosphazine, $(C_6H_4)_2C{=}N{-}N{=}P(C_6H_5)_3$, at its melting point, 209°; also, from fluorenone phenyldiethylphosphazine and from benzophenone phenyldiethylphosphazine.[78] With benzophenone triphenylphenylphosphazine at 185-190° in nitrogen atmosphere, the equation is:

$$(C_6H_5)_3P{=}N{-}N{=}C(C_6H_5)_2 \longrightarrow N_2 + (C_6H_5)_3P{=}C(C_6H_5)_2.$$

Ammonia is one of the products of pyrolysis from bi-diphenyltetrahydrotetrazine, $(C_6H_5)_2C{<}\begin{matrix} N{-}\!\!-\!\!-N \\ NH{-}NH \end{matrix}{>}C(C_6H_5)_2$.

DIAZO AND AZIDO COMPOUNDS.

It is well known that the aliphatic analogs of benzenediazonium hydroxide are incapable of existence. Invariably, in attempts to secure them [79] they become further dehydrated:

$$[CH_3{-}N{=}NOH] \longrightarrow CH_2N_2 + H_2O.$$

Above 200°, diazomethane [80] may explode violently into ethylene and nitrogen, although it has been employed in the synthesis of ketene: [81]

$$CH_2N_2 + CO \longrightarrow CH_2{=}CO + N_2,$$

at considerably higher temperatures than this (400-500°).

[78] Staudinger and Meyer, *Helv. Chim. Acta* **2**, 619 (1919).
[79] Hantzsch and Lehmann, *Ber.* **35**, 897 (1902).
[80] von Pechmann, *Ber.* **31**, 2643 (1898).
[81] Staudinger and Kupfer, *Ber.* **45**, 508 (1912).

Reactions which were intended [82] to synthesize an isomer of diazomethane, $\begin{matrix} CH{=}N \\ \diagdown\ \diagup \\ NH \end{matrix}$, always gave instead, $3HCN + NH_3 + N_2$.

Phenyl-diazomethane, $C_6H_5CH{=}N_2$, decomposes [83] for the most part by distilling at ordinary pressure. Nitrogen is liberated and there remains a residue of stilbene. Diazomethane itself also pyrolyzes similarly, giving ethylene and nitrogen. With more complex derivatives of diazomethane, there are two other modes of pyrolysis, one leading to the formation of ketazines and the other to products of rearrangement.

(1) $2CH_2{=}N_2 \longrightarrow 2N_2 + CH_2{=}CH_2$

(2) $2Ar_2C{=}N_2 \longrightarrow N_2 + Ar_2C{=}N{-}N{=}CAr_2$

(3) $C_6H_5CO{-}CN_2{-}C_6H_5 \longrightarrow N_2 + [C_6H_5CO{-}\underset{\diagup\ \diagdown}{C}{-}C_6H_5] \longrightarrow (C_6H_5)_2C{=}C{=}O.$

Diphenyldiazomethane,[84] $(C_6H_5)_2C{=}N_2$, melts at 29-30°, and gradually decomposes into the ketazine. It explodes at about 115°. It might be anticipated that this aliphatic diazo compound would decompose briskly in boiling xylene, and such is the case. This is also true [85] with phenyl-diazomethane, phenylmethyl-diazomethane, diphenylene-diazomethane, dibenzoyl-diazomethane, diacetyl-diazomethane, and azibenzil (benzoyl-phenyl-diazomethane). The latter three substances decompose violently in hot xylene. Phenyl-diazomethane has a "life" of a few days, but diphenylene-diazomethane may be kept for months.

Di-*p*-tolyldiazomethane,[86] on boiling in benzene or heating *in vacuo*, changes into the ketazine:

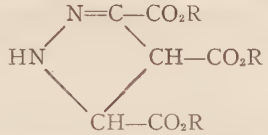
$$2(CH_3C_6H_4)_2C{=}N_2 \longrightarrow N_2 + (CH_3C_6H_4)_2C{=}N{-}N{=}C(C_6H_4CH_3)_2.$$

p-Tolyl-phenyl-diazomethane undergoes pyrolysis into the ketazine at the melting point, 53-55°, and di-*p*-bromophenyl-diazomethane changes rapidly into the corresponding ketazine in boiling benzene. Obviously, the isolation of the ketazines depends on the fact that the pyrolysis is performed at a temperature sufficiently low to permit of the isolation of the ketazines.

Ethyl diazoacetate undergoes pyrolysis in attempts to purify it by distillation [87] at ordinary pressure; it may be distilled in steam or in a vacuum, however. At temperatures above 150°, ethyl fumarate is the product of the pyrolysis:

$$2N_2{=}CH{-}CO_2C_2H_5 \longrightarrow 2N_2 + (=CH{-}CO_2C_2H_5)_2.$$

[82] Hantzsch and Lehmann, *Ber.* **34**, 2506 (1901).
[83] Hantzsch and Lehmann, *Ber.* **35**, 904 (1902).
[84] Staudinger, Anthes and Pfenninger, *Ber.* **49**, 1928 (1916).
[85] Staudinger and Gaule, *Ber.* **49**, 1897 (1916).
[86] Staudinger and Goldstein, *Ber.* **49**, 1923 (1916).
[87] Curtius and Jay, *J. prakt. Chem.* [2] **39**, 55 (1889).

If the heating is carried out at 120-130°, three-fourths of the nitrogen is evolved [88] in about 28 hours, giving a mixture consisting chiefly of ethyl pyrazoline-3,4,5-tricarboxylate,  , a trace of ethyl fumarate, and ethyl cyclopropane-tricarboxylate. These products are supposed to be produced as the result of the following reactions: a portion of the diazoacetate is converted into the fumarate, which then condenses [89] with unchanged diazo-ester, a portion of which then undergoes pyrolysis into the cyclopropane derivative. Triethyl *trans*-cyclopropane-1,2,3-tricarboxylate may be prepared by heating the pyrazoline tricarboxylate. The methyl ester behaves analogously.

The reaction kinetics [90] of the decomposition of ethyl diazoacetate have been studied, and, when heated adiabatically, have been found to be in agreement with Bredig and Epstein's equation. Curtius and Müller [91] have found that ethyl dimethylfumarate may be synthesized by heating ethyl α-diazopropionate.

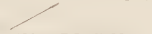
The reaction product [92] of diphenylene diazomethane and ethyl azodicarboxylate, namely, ethyl hydrazifluorenedicarboxylate, rearranges into ethyl fluorenonehydrazone-dicarboxylate at 150-180°:

$$C_{12}H_8{=}C{<}\begin{matrix}N{-}CO_2Et\\ |\\ N{-}CO_2Et\end{matrix} \longrightarrow C_{12}H_8{=}C{=}N{-}N(CO_2Et)_2.$$

Derivatives of ethyl diazoacetate, such as ethyl benzoyldiazoacetate, $C_6H_5CO{-}CN_2{-}CO_2C_2H_5$, if heated alone [93] at 250° give ethyl phenylmalonate, $C_6H_5CH(CO_2Et)_2$; but if the methyl ester is boiled with xylene, nitrogen is quantitatively evolved and the polymer of the ketene remains. This, on distillation, depolymerizes into methyl phenylketenecarboxylate, $O{=}C{=}C(C_6H_5){-}CO_2CH_3$. Similarly, diethyl ketenedicarboxylate, $OC{=}C(CO_2Et)_2$, may be formed by heating $EtO_2C{-}CO{-}CN_2{-}CO_2Et$ in xylene, whereas this ketene is admixed with $HC(CO_2Et)_3$ if the diazo-ester is heated alone at 250°. A like con-

[88] Curtius, *Ber.* **18**, 1302 (1885); Darapsky, *Ber.* **43**, 1121 (1910).

[89] For the reaction of ethyl fumarate and diphenylene-diazo-methane, giving ethyl 1-diphenylene-cyclopropane-2,3-dicarboxylate, *see* Staudinger and Gaule, *Ber.* **49**, 1951 (1916). Staudinger, Anthes and Pfenninger, *ibid.* p. 1928, discuss the synthesis of ethyl 5,5-diphenyl-pyrazoline-3,4-dicarboxylate, $(C_6H_5)_2C{-}NH{-}N{=}C{-}CO_2C_2H_5$, from ethyl fumarate and di-



phenyldiazomethane; at 190-200°, this pyrazoline derivative changes quantitatively into ethyl 1,1-diphenylcyclopropane-2,3-dicarboxylate and nitrogen.

[90] Lachs, *Chem. Abstracts* **6**, 17 (1912).

[91] Curtius and Müller, *Ber.* **37**, 1272 (1904).

[92] Staudinger and Gaule, *Ber.* **49**, 1961 (1916).

[93] Staudinger and Hirzel, *Ber.* **49**, 2522 (1916).

version [94] of ethyl α-diazoacetoacetate, $CH_3—CO—CN_2—CO_2Et$, into ethyl methylmalonate, $CH_3—CH(CO_2Et)_2$, occurs at about 110°.

A very useful pyrolytic reaction is the one which is used in the synthesis of diphenyl ketene [95] from azibenzil:

$$C_6H_5—CO—\underset{\underset{N_2}{\|}}{C}—C_6H_5 \longrightarrow N_2 + (C_6H_5)_2C=C=O.$$

In this method, the intermediate is benzil, or more remotely, benzaldehyde. It becomes, then, the best method of synthesis for this important ketene. The details of the procedure consist merely in warming a solution of azibenzil in benzene to 60° or higher. Although nitrogen is evolved, this is insufficient to exclude atmospheric oxygen; therefore, a carbon dioxide atmosphere is usually provided. Pure azibenzil melts [96] at 63° with some decomposition. Schroeter mentioned 110-120° as the decomposition temperature. In the preparation of diphenyl ketene, the isolation of azibenzil should be avoided,[97] and if care is taken, yields of 70 percent may be attained.

The rearrangement of azibenzil into diphenyl ketene is parallel to that of benzazide into phenyl *iso*cyanate:

$$C_6H_5—CO—\underset{\underset{C_6H_5}{|}}{C}=N\equiv N \longrightarrow (C_6H_5)_2C=C=O + N_2$$

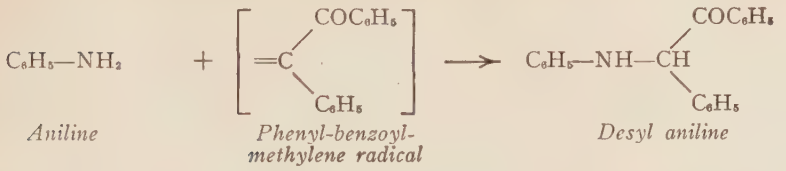
$$C_6H_5—CO—N=N\equiv N \longrightarrow C_6H_5—N=C=O + N_2.$$

Because of the similarity in the structure of azibenzil and diazomethane, and because of the known excellence of the latter substance as a methylating agent, experiments were recently carried out [98] in the author's laboratory to see if azibenzil might be utilized as a "benzoinating" agent. In other words, the experiments were designed to learn whether or not the phenyl-benzoyl-methylene radical actually is an intermediate product, and if so, to attach it to an active compound, prior to rearrangement. This condition was realized by performing the pyrolysis in the presence of benzoic acid or of aniline:

$$C_6H_5—CO—OH + \left[\begin{array}{l} COC_6H_5 \\ =C \\ C_6H_5 \end{array}\right] \longrightarrow \begin{array}{l} COC_6H_5 \\ C_6H_5—CO—O—CH \\ C_6H_5 \end{array}$$

Benzoic acid — *Phenyl-benzoyl-methylene radical* — *Benzoin benzoate*

[94] Wolff, *Ann.* **325**, 136 (1902); **394**, 27 (1912); Schroeter, *Ber.* **42**, 2347 (1909).
[95] Schroeter, *Ber.* **42**, 2345 (1909).
[96] Curtius and Thun, *J. prakt. Chem.* **44**, 182 (1891).
[97] Staudinger, *Ber.* **44**, 1622 (1911).
[98] Hurd and Bennett, unpublished data.



The yields of these "benzoinated" substances are very small but nevertheless quite definite. With the benzoic acid experiment, diphenyl ketene is also formed, and with the aniline experiment, diphenyl-acetanilide.

Methyl azide, $CH_3—N_3$, decomposes with explosive violence [99] above 500°. Cyanogen azide detonates [100] at 170-180°. Tetramethyl-tetrazone, $(CH_3)_2N—N=N—N(CH_3)_2$, is volatile in steam, but it explodes [101] at higher temperatures.

A solution (4 percent) of hydrogen azide, if maintained [102] at 230° for 48 hours, undergoes a partial change into ammonium azide. About one-third of the HN_3 remains intact. Presumably the course of the reaction takes the following steps:

$$3HN_3 \longrightarrow 3N_2 + 3[H—N=]$$

$$\downarrow$$

$$NH_3 + N_2$$

$$HN_3 + NH_3 \longrightarrow NH_4N_3.$$

In a condensed equation, this becomes :

$$4HN_3 \longrightarrow NH_4N_3 + 4N_2.$$

No nitrogen is evolved from *benzyl azide* as it is boiled in xylene solution, but if the solution is heated [103] in an autoclave at 170-180°, ammonium azide results, due to a prior dissociation into hydrogen azide. The compounds benzdibenzylamidine, $C_6H_5—C(=N—CH_2C_6H_5)—NH—CH_2C_6H_5$; tribenzylamine; tetraphenylpyrazine (amaron), $C_6H_5—C(=N—C(=C—C_6H_5)—C_6H_5)—C_6H_5$; and benzyldiphenylpyrrodiazole, $C_6H_5—C(=N—N)—C(—C_6H_5)$ with $N—CH_2C_6H_5$ closing the ring, are also isolable.

[99] Dimroth and Wislicenus, *Ber.* **38**, 1576 (1905).
[100] Darzens, *Compt. rend.* **154**, 1232 (1912); Hart, *J. Am. Chem. Soc.* **50**, 1922 (1928).
[101] Angeli and Angelico, *Atti. accad. Lincei*, [5] **10**, I, 167 (1901); Angeli and Castellana, *ibid.* **14**, I, 272 (1905).
[102] Bertho, *Ber.* **59**, 589 (1926).
[103] Curtius and Ehrhart, *Ber.* **55**, 1559 (1922).

To explain these results, Curtius postulates a two-fold scission of the azide:

(1) $C_6H_5—CH_2—N=N_2 \longrightarrow [C_6H_5—CH_2—N=] + N_2$

(2) $C_6H_5—CH_2—N_3 \longrightarrow [C_6H_5—CH=] + HN_3$.

Then:

$$[C_6H_5—CH_2—N=] + [C_6H_5—CH=] \longrightarrow C_6H_5—CH_2—N=CHC_6H_5$$

$$C_6H_5—CH_2—N=CHC_6H_5 + [C_6H_5—CH_2—N=] \longrightarrow C_6H_5—\underset{\underset{N—CH_2C_6H_5}{\|}}{C}—NH—CH_2C_6H_5$$

To explain the formation of the pyrrodiazole and the tribenzylamine, it is suggested that the radical $[C_6H_5—CH_2—N=]$ rearranges into $[C_6H_5CH=NH]$, which then becomes dehydrogenated into

$$[C_6H_5—\underset{|}{C}=N—].$$

The hydrogen atoms reduce $[C_6H_5—CH=]$ to benzyl, two of which combine with one of $[C_6H_5—CH_2—N=]$ giving tribenzylamine. Simultaneously, $2[C_6H_5—\underset{|}{C}=N—]$ radicals are thought to combine with themselves, giving $[—C(C_6H_5)=N—N=C(C_6H_5)—]$, which, with $[C_6H_5—CH_2—N=]$, yields the pyrrodiazole. None of the residues is actually isolable.

At 150-160°, only one of the azide groups in benzophenone diazide,[104] $(C_6H_5)_2C<\begin{matrix}N_3\\N_3\end{matrix}$, is eliminated as nitrogen. The pyrolysis proceeds as follows:

$$(C_6H_5)_2\underset{\underset{N_3}{|}}{C}—N_3 \longrightarrow N_2 + \left[(C_6H_5)_2\underset{|}{C}—N_3 \longrightarrow (C_6H_5)_2C{=}N—\right] \longrightarrow C_6H_5—\underset{\underset{C_6H_5—N}{\|}}{C}—N_3 \longrightarrow$$

$$C_6H_5—C=N$$
$$\qquad\quad |\quad\ \backslash$$
$$\qquad\quad |\qquad N.$$
$$\qquad\quad |\quad\ /$$
$$C_6H_5—N—N$$

Rearrangements of this type which involve the transfer of a radical from carbon to nitrogen are often broadly classified as the Beckmann rearrangement.

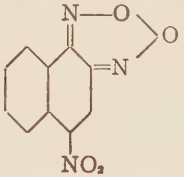
Tetramethylammonium azide [105] begins to evolve vapors of fishy odor at 125°. In this process, there is no indication of a molecular transposition to tetramethyl-tetrazone, $(CH_3)_2N—N=N—N(CH_3)_2$.

Phenyl azide [106] undergoes pyrolysis at 150-160° in benzene solution,

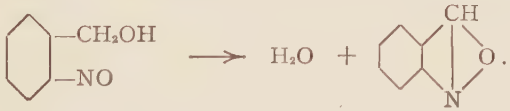
[104] Schroeter, *Ber.* **42**, 2342, 3359 (1909).
[105] Friedlander, *J. Am. Chem. Soc.* **40**, 1945 (1918).
[106] Bertho, *Ber.* **57**, 1138 (1924).

without interaction with the solvent. With xylene, there is interaction. In benzene, the decomposition leads to the formation of azobenzene and nitrogen, together with a little aniline. The decomposition proceeds through a "rigid residue", $[C_6H_5—N=]$, which is capable of reacting with some hydrocarbons, or which may polymerize.

The effect of gradually raising the temperature [107] to about 110° on *o*-nitrophenyl azide, and related compounds, is to produce benzofuroxane-oxide.

2,4-Dinitronaphthyl-azide loses nitrogen [108] by fusion (105°) or by heating for 6 hours in xylene, with the resultant formation of 4-nitro-1,2-naphthoquinone-dioxime peroxide,  . The effect of the "rigid residue" is apparent also in the pyrolytic preparation of anthranil [109] from *o*-azido-benzaldehyde:

Anthranil [110] may also be formed by heating *o*-nitrosobenzyl alcohol in hot water:



Diazonium Salts.

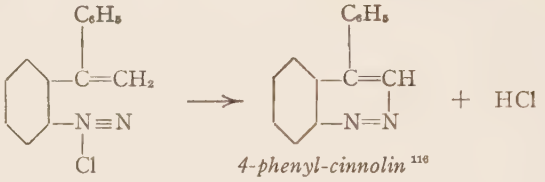
Nearly all diazonium salts may explode on heating in the dry state. Diazobenzene nitrate is particularly unstable,[111] and nitro groups (in the nucleus) occasion still greater instability. A case is on record where benzenediazonium chloride, usually regarded as comparatively stable,

[107] Noelting, Grandmougin and Michel, *Ber.* **25**, 3339 (1892); Zincke, *J. prakt. Chem.* **53**, 340 (1896); Drost, *Ann.* **307**, 46 (1899); Foerster and Fierz, *J. Chem. Soc.* **91**, 1943 (1907); Foerster and Barker, *ibid.* **103**, 1918 (1913).
[108] Muller and Weisbrod, *J. prakt. Chem.* **113**, 30 (1926).
[109] Bamberger and Demuth, *Ber.* **34**, 3874 (1901).
[110] Bamberger, *Ber.* **36**, 839 (1903).
[111] Knoevenagel, *Ber.* **23**, 2994 (1890); Bamberger, *Ber.* **28**, 538 (1895).

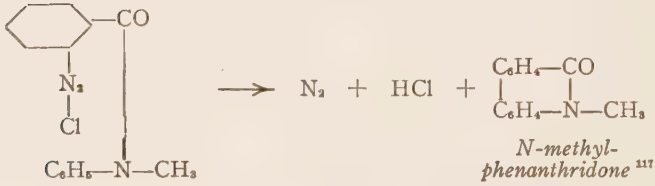
exploded spontaneously [112] and violently. Benzenediazonium nitrate [113] explodes above 90°, and *m*- and *p*-nitrobenzenediazonium chlorides [114] at 118° and 85° respectively.

The decomposition of benzenediazonium chloride in hot water solution is not a pyrolysis, but it is interesting to record that phenol is not the exclusive product. Fair yields of phenyl chloride [115] are also formed. As is well known, this decomposition may be profoundly affected by catalysts.

The following reactions, which are less well known, proceed in the acid solution, the first at ordinary temperatures and the second on warming:



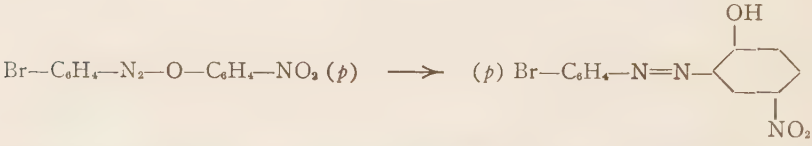
4-phenyl-cinnolin [116]



N-methyl-phenanthridone [117]

Benzoyl-1-aminonaphthalene-4-diazonium azide [118] loses nitrogen at 0°, as it becomes transformed into benzoyl-1-aminonaphthyl-4-azoimide, $C_6H_5CO—NH—C_{10}H_6N_3$.

In the dry state, the following rearrangement occurs at 80°:



Dimroth prefers [119] the diazototate structure, whereas von Auwers considers the nitrogens in the original compound to be of the diazonium type.

[112] Hantzsch, *Ber.* **30**, 2342 footnote (1897).
[113] Berthelot and Vielle, *Compt. rend.* **92**, 1074 (1881).
[114] Oddo, *Gazz. chim. ital.* **25**, I, 327 (1895).
[115] Gasiorowski and Wayss, *Ber.* **18**, 337, 1936 (1885).
[116] Stoermer and Fincke, *Ber.* **42**, 3116 (1909). *See* Stoermer and Gaus, *Ber.* **45**, 3104 (1912), for a similar reaction.
[117] Pictet and Gonset, *Chem. Zentr.* **1897**, I, 414.
[118] Morgan and Couzens, *J. Chem. Soc.* **97**, 1691 (1910).
[119] Dimroth, *Ber.* **41**, 4012 (1908); von Auwers, *Ber.* **41**, 4304 (1908); Bucherer, *Ber.* **42**, 47 (1909).

CHAPTER 22.

NITRO COMPOUNDS; HYDROXYLAMINE AND RELATED SUBSTANCES; REARRANGEMENTS OF THE BECKMANN, LOSSEN, HOFMANN AND CURTIUS TYPES.

Nitro Compounds.

Chloropicrin decomposes [1] at the rate of 2 cc. per day, when 200 gram samples are maintained at the boiling point. The products of the decomposition are phosgene and nitrosyl chloride:

$$CCl_3NO_2 \longrightarrow COCl_2 + NOCl.$$

Bromonitromalonic methyl (or ethyl) ester [2] smoothly liberates nitrosyl bromide on heating:

$$(RO_2C)_2C<^{Br}_{NO_2} \quad or \quad (RO_2C)_2C<^{O}_{N—OBr} \longrightarrow (RO_2C)_2CO + NOBr.$$

Much the same behavior [3] is reported in the case of *o*-bromophenylbromonitroacetamide, $BrC_6H_4—CBr(NO_2)—CONH_2$, which changes into *o*-bromobenzoyl cyanide and nitrosyl bromide.

Most nitroso compounds rearrange spontaneously into the *iso*nitroso compounds, or oximes. One case to illustrate [4] this is:

$$CH_3—CHCl—NO \longrightarrow CH_3—CCl{=}NOH.$$

See later, page 754.

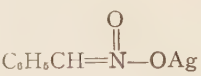
The sodium salts of nitroparaffins [5] explode on heating. This is also true with the potassium salt [6] of chlorodinitromethane (at 83°). The sodium or potassium or ammonium salts of nitroform gradually decompose in the dry state in accordance with the following equation: [7]

$$2(O_2N)_2C{=}\underset{\underset{O}{\|}}{N}—ONa \longrightarrow 2NaNO_3 + 2CO_2 + 2NO + N_2.$$

[1] Gardner and Fox, *J. Chem. Soc.* **115**, 1188 (1919).
[2] Willstätter and Hottenroth, *Ber.* **37**, 1781 (1904).
[3] Wislicenus and Fischer, *Ber.* **43**, 2240 (1910); Flürscheim and Holmes, *J. Chem. Soc.* **1928**, 453.
[4] Piloty and Steinbock, *Ber.* **35**, 3114 (1902).
[5] Zelinsky, *Ber.* **27**, 3406 (1894).
[6] Gotts and Hunter, *J. Chem. Soc.* **125**, 442 (1924)
[7] Hantzsch and Rickenberger, *Ber.* **32**, 628 (1899).

Above 150°, the ammonium salt of diphenyl-*iso*nitromethane [8] pyrolyzes into benzophenone.

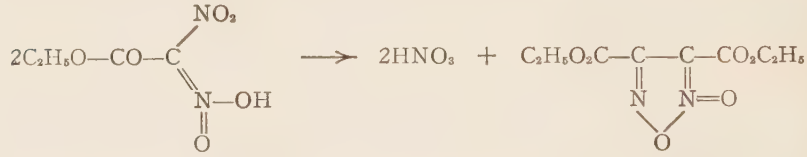
Among the silver salts,[9] silver phenyl-*iso*nitromethane,



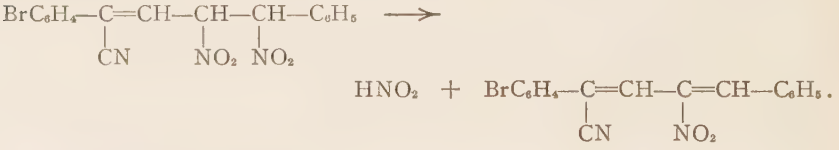
decomposes into α-dinitrostilbene; and silver nitrosophenylhydroxylamine,[10] C_6H_5—N(NO)—OAg, turns brown with deposition of silver and the formation of nitrosobenzene and nitric oxide.

Dinitro Compounds.

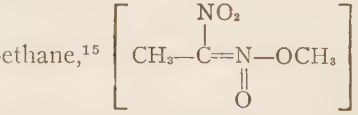
Peculiarly, dinitromethane [11] exists for only a few seconds even at −15°, whereas α,α-dinitrobutane [12] may be distilled at 197° with only a partial decomposition. Ethyl dinitroacetate [13] undergoes a ring closure by warming. This occurs gradually even at room temperature with the production of ethyl furoxan-dicarboxylate:



If α-cyano-α-*p*-bromophenyl-γ,δ(?)-dinitro-δ-phenyl-α-butylene [14] is melted (128°), it rapidly evolves nitrous acid and yields α-cyano-α-*p*-bromophenyl-γ(?)-nitro-δ-phenyl-α,γ-butadiene:



In other words, nitrous acid is liberated much in the manner that hydrogen bromide is detached from alkyl bromides.

The *O*-methyl ether of dinitroethane,[15]  , is incapable of existence, but breaks down with the liberation of formalde-

[8] Konowalow, *Chem. Zentr.* **1900**, I, 1092.
[9] Angeli and Alessandri, *Atti accad. Lincei* **19**, I, 784 (1910).
[10] Angeli, Castellana and Ferrero, *ibid.* **18**, II, 38 (1909).
[11] Duden, *Ber.* **26**, 3005 (1893).
[12] Chancel, *Compt. rend.* **96**, 1466 (1883).
[13] Wahl, *Ann. chim.* [8] **25**, 429 (1912).
[14] Neber and Paeschke, *Ber.* **59**, 2140 (1926).
[15] Nef, *Ann.* **280**, 283 (1894).

hyde and the nitrolic acid, $CH_3—\overset{NO_2}{\overset{|}{C}}=NOH$. This may be compared to the pyrolysis of alkyl hyponitrites into aldehydes (p. 634). At the melting point of ethyl nitrolic acid (86°), it undergoes pyrolysis [16] with a stormy evolution of gas:

$$2CH_3—C(NO_2)=NOH \longrightarrow 2CH_3CO_2H + NO_2 + 1.5N_2.$$

Somewhat different from this is the formation of dibenzoyl-glyoxime-peroxide [17] in the following reaction, which takes place in a vacuum:

$$2C_6H_5CO—C(NO_2)=NOH \longrightarrow H_2O + C_6H_5CO(C_2N_2O_2)—COC_6H_5.$$

Methyl nitrosolic acid [18] yields fulminic acid:

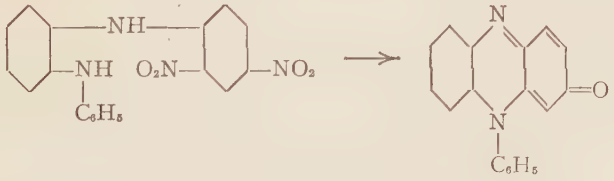
$$2H—\overset{NO}{\overset{|}{C}}=NOH \longrightarrow [H_2N_2O_2] + 2HONC.$$
$$\qquad\qquad\qquad\qquad\quad \downarrow$$
$$\qquad\qquad\qquad\qquad\quad N_2O + H_2O$$

An interesting transformation [19] of monobromo-trimethylethylene-nitrosate into bromonitroethyl-*iso*propyl nitrate occurs with good yields at 140-150°. Nitrous fumes are also liberated as the blue crystalline substance changes into the colorless one:

$$(CH_3)_2\overset{ONO_2}{\overset{|}{C}}—\overset{NO}{\overset{|}{C}}Br—CH_3 \longrightarrow (CH_3)_2\overset{ONO_2}{\overset{|}{C}}—\overset{NO_2}{\overset{|}{C}}Br—CH_3$$

It is known that benzamidoxime,[20] $C_6H_5—\overset{NH_2}{\overset{|}{C}}=NOH$, yields benzonitrile by quick heating to 170°. The elements of hydroxylamine are not liberated as such, but appear as nitrogen and ammonia.

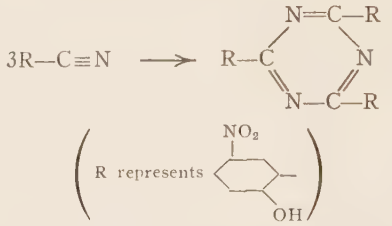
The simple aromatic nitro compounds have been neglected for their behavior under pyrogenic influences. Undoubtedly, at sufficiently elevated temperatures, the nitro group would exert a considerable oxidizing effect. The following conversion is brought about by heating in benzoic acid or in benzil: [21]



[16] Meyer, *Ann.* **175**, 104 (1875); Behrend and Tryller, *Ann.* **283**, 245 (1895).
[17] Ruggeri, *Atti accad. sci. Torino* **59**, 705 (1921); *Chem. Abstracts* **19**, 469.
[18] Wieland and Hess, *Ber.* **42**, 4176 (1909).
[19] Schmidt and Austin, *Ber.* **36**, 1768 (1903).
[20] Krüger, *Ber.* **18**, 1054 (1885).
[21] Kehrmann and Messinger, *J. prakt. Chem.* [2] **46**, 572 (1892).

It is not the customary thing to regard benzil or benzoic acid as "neutral solvents", but such is the claim for them in this case.

If 2-hydroxy-5-nitro-benzonitrile [22] is held above its melting point (190°) for a brief period, there is formed 2,4,6-tri-(2-hydroxy-5-nitrophenyl)-1,3,5-triazine. In this reaction, however, the nitro group is inert, and the final compound is a trimer of the original one:



A similar polymerization into 2,4,6-tri-(2-hydroxy-3,5-dibromophenyl)-1,3,5-triazine occurs on fusing 3,5-dibromosalicylonitrile (see p. 603).

Hydroxylamine and Related Compounds.

Hydroxylamine occupies an intermediate position in the nitrogen scale of valence. This is reflected in its pyrolysis, which assumes the nature of a simultaneous oxidation and reduction. Ammonia is the reduction product, and nitrogen or nitrous oxide are the oxidation products as *hydroxylamine hydrochloride* [23] is heated to 150° in an atmosphere of carbon dioxide:

$$3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$$
$$4NH_2OH \longrightarrow N_2O + 2NH_3 + 3H_2O.$$

The mechanism of this decomposition is considered to proceed through a transitory molecule of β,β-diamino-hydroxylamine:

$$3NH_2OH \longrightarrow 2H_2O + \left[HO—N<\begin{matrix}NH_2\\NH_2\end{matrix}\right].$$

Bases (aniline, ammonia, potassium bicarbonate) favor its decomposition into nitrogen, by the following reaction:

$$[HO—N(NH_2)_2] + H_2O \longrightarrow [HO—N=O + 2NH_3]$$
$$[HO—N(NH_2)_2] + H_2O \longrightarrow [NH_4NO_2] + NH_3$$
$$\downarrow$$
$$N_2 + 2H_2O$$

[22] Lindemann and Thiele, *Ann.* **449**, 72 (1926).
[23] Hofmann and Kroll, *Ber.* **57**, 937 (1924).

Acidic substances, on the other hand, such as the hydrates of aluminum chloride and zinc chloride, phosphoric acid, sulfuric acid, and especially potassium bisulfate, favor the decomposition into nitrous oxide:

$$[HO{-}N(NH_2)_2] + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + ON{-}O{-}SO_3H$$
$$NH_2OH + ON{-}O{-}SO_3H \longrightarrow N_2O + H_2SO_4.H_2O.$$

Oximes.

Some Oxime Reactions.

Gradual heating of *syn*-benzaldoxime [24] induces the transformation into the *anti* form. More vigorous heating will cause a dehydration to the nitrile, a reaction which is customarily performed, however, with a dehydrating agent. The following change from aldoxime to nitrile is effected [25] by distillation:

$$HON{=}CH{-}\underset{\displaystyle CH_2{-}CO_2C_2H_5}{\underset{|}{CH}}{-}CO_2C_2H_5 \longrightarrow N{\equiv}C{-}\underset{\displaystyle CH_2{-}CO_2C_2H_5}{\underset{|}{CH_2}} + C_2H_5OH + CO_2.$$

Apparently, therefore, the molecule of water from the oxime induces hydrolysis of an ester grouping, immediately to be followed by the pyrolytic detachment of the carboxyl group. An alternative mechanism is to assume the formation of an unstable isoxazolone by the elimination of alcohol. This would bring the result in harmony with Zanetti and Beckmann's [25a] results with the oximes of furoylacetic esters which give furyl-isoxazolone at the melting point, (100-120°):

$$C_4H_3O{-}\underset{\displaystyle N{-}O{-}H}{\underset{\|}{C}}{-}CH_2{-}CO_2R \longrightarrow C_4H_3O{-}\underset{\displaystyle N{-}\!-\!-\!-O}{\underset{\|}{C}}{-}\underset{|}{CH_2}{-}CO + H_2O.$$

In this connection, it is interesting to point out that neither ethyl acetoacetate nor ethyl benzoacetate gives a stable oxime.

Both ammonia and water are eliminated [26] from the aldoxime of 4,6-dicarbethoxyl-5-formyl-3-methyl-Δ^2-cyclohexenone,

$$CH_3{-}\underset{\displaystyle CH{-}CO{-}CH{-}CO_2Et}{\underset{\|}{C}}{-}\underset{\displaystyle CO_2Et}{\underset{|}{CH}}{-}\underset{|}{CH}{-}CH{=}NOH$$

by heating it for 20-30 minutes at 100°. The source of the ammonia was not mentioned, but it may have resulted from a hydrolysis of the nitrile.

[24] Beckmann, *Ber.* **20**, 2768 (1887); **23**, 1685 (1890); Behrend and König, *Ann.* **263**, 356 (1891).
[25] Carrière, *Ann. chim.* **17**, 38 (1921).
[25a] Zanetti and Beckmann, *J. Am. Chem. Soc.* **50**, 1438 (1928).
[26] West, *J. Am. Chem. Soc.* **47**, 2786 (1925).

Acetone oxime is reported [27] to change at 200-270° (6 hours in a sealed tube) into methane and a mixture of bases which includes ammonia. In this, and in the cases to follow, the Beckmann rearrangement never occurs. Benzoic acid, acetophenone and possibly methane are the pyrolytic reaction products from acetophenone oxime. Phenyl-benzyl-ketoxime explodes at 270°, and in the products of decomposition are ammonia, benzonitrile, desoxybenzoin, benzyl alcohol and lophine. Benzoin oxime yields benzaldehyde, benzonitrile and lophine at 240°. It will be noticed that in the oximes of benzoin and desoxybenzoin, there is tendency for fission to the nitrile:

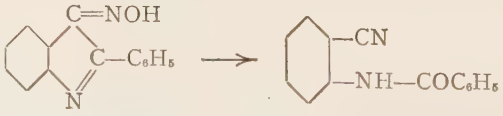
$$\mathrm{R{-}C(=N{-}OH){-}R' \longrightarrow R{-}C{\equiv}N + R'{-}OH}$$

This type of pyrolysis [28] may be realized very excellently from α- or γ-benzil monoxime. The α-oxime melts at 134°; at 200°, a vigorous exothermic reaction occurs, and the temperature of the mixture rises fifty degrees:

$$\mathrm{C_6H_5{-}C(=NOH){-}COC_6H_5 \longrightarrow C_6H_5CN + C_6H_5CO_2H}.$$

If the α-oxime is kept for 1 or 2 hours at its melting point, it rearranges into the γ-oxime. Benzil dioximes will be discussed later. *o*-Methoxy-phenyl-phenyl-ketoxime [29] melts at 158°, and thereby changes into the isomeric oxime of melting point, 130°.

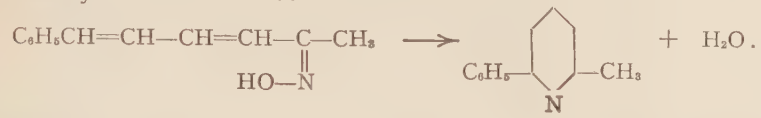
If cyclohexanone oxime is boiled for an hour (Kötz and Wunstorf) considerable of the oxime is recoverable, but a brown resin is indicative of pyrolysis of some sort. Nitrosophenylindole melts (258°) without giving any 2-phenylindolone, but a small yield [30] of *o*-benzoylamino-benzonitrile indicates the opening of the heterocyclic ring without further change:



During the decomposition, a gas escapes which liberates iodine from starch-iodide paper. This effect ceases at 270-280°.

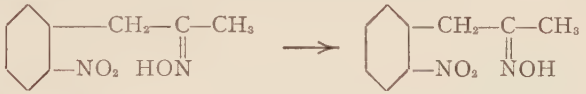
[27] Kötz and Wunstorf, *J. prakt. Chem.* **88**, 519 (1913).
[28] Beckmann and Köster, *Ann.* **274**, 6 (1893).
[29] Billon, *Ann. chim.* **7**, 332 (1927).
[30] Alessandri, *Atti accad. Lincei* **22**, II, 150 and 227 (1913).

The formation of phenylmethylpyridine [31] is the result of distillation of cinnamylidene-acetoxime:



Homologs with this unsaturated chain also pyrolyze similarly.

o-Nitrobenzyl methyl ketoxime furnishes another example [32] of the rearrangement. of the labile form of a ketoxime into the stable isomer by heating. The β-isomer (*syn*) is very sweet; the α- or *anti*-isomer is tasteless. The latter (melting point 158°) is prepared by gently heating the former above its melting point, 151°:



Benzophenone Oxime.

Benzophenone oxime has been more thoroughly investigated than any other. Both Angeli [33] and Kötz and Wunstorf (*loc. cit.*) reported the identification of benzophenone, nitrogen and ammonia at temperatures of 170-180°. Lachman, however, found diphenylmethane-imine [34] among the products from this pyrolysis (185°). He considered that a nitroxyl group was eliminated, according to the following equation:

$$2(C_6H_5)_2C{=}NOH \longrightarrow (C_6H_5)_2C{=}O + (C_6H_5)_2C{=}NH + [NOH];$$

and then, [NOH] gives rise to nitrogen, nitrous oxide and water. Almost exactly half of the nitrogen in this nitroxyl residue appears as nitrogen gas. The water induces a partial hydrolysis of the imine:

$$(C_6H_5)_2C{=}NH + H_2O \longrightarrow (C_6H_5)_2C{=}O + NH_3.$$

There is no trace of benzanilide, the product which would be the result of a Beckmann rearrangement.

Quite different results come by heating the hydrochloride of benzophenone oxime. This substance [35] melts at 128° with an evolution of hydrogen chloride. Suddenly, the liquid solidifies and there results a 95 percent yield of benzanilide. Lehmann [36] found that the rearrangement was practically complete after a time at 110°, and Lachman

[31] Scholtz, *Ber.* **28**, 1726 (1895); **32**, 1935 (1899); Scholtz and Wiedemann, *Ber.* **36**, 845 (1903); Scholtz and Meyer, *Ber.* **43**, 1861 (1910).
[32] Neber and others, *Ber.* **58**, 1234 (1925).
[33] Angeli, *Atti accad. Lincei* **21**, I, 83 (1912).
[34] Lachman, *J. Am. Chem. Soc.* **46**, 1477 (1924).
[35] Kuhara, *Mem. Coll. Sci. Kyoto Imp. Univ.* **3**, No. 1, 1 (1917); *Chem. Abstracts* **13**, 119 (1919).
[36] Lehmann, *Z. angew. Chem.* **36**, 360 (1923).

(*loc. cit.*) demonstrated the catalytic nature of the hydrogen chloride. As little as 0.04 mol of it will effect almost a complete conversion in one hour at 160°, since it is constantly being liberated and reused:

$$(C_6H_5)_2C{=}NOH.HCl \longrightarrow C_6H_5CO{-}NHC_6H_5 + HCl.$$

Another acidic substance which is related to benzophenone oxime is prepared by allowing the oxime to react in ether solution with phosphorus pentasulfide, P_2S_5, and phosphorus pentoxide, P_2O_5. In the dry state, this compound,[37] $((C_6H_5)_2C{=}N{-}S{-})_2PO{-}OH$, decomposes explosively at 70°, giving thiobenzanilide, $C_6H_5CS{-}NHC_6H_5$.

The hydrochloride of acetyl-benzophenone oxime, $(C_6H_5)_2C{=}N{-}OCOCH_3.HCl$, does not rearrange[35] above its melting point, but instead methyl chloride is evolved. Mesityl-oxide-oxime-hydrochloride, $(CH_3)_2C{=}CH{-}\underset{\underset{NOH.HCl}{\|}}{C}{-}CH_3$, melts at 62°, and changes[38] at 80° into the more stable isomer, which in turn melts with decomposition at 123°.

It would seem that Lachman's mechanism of the formation of benzanilide from benzophenoneoxime-hydrochloride could be used to explain the formation of anilides[39] from the interaction of the "imine residue" (produced by the interaction of HN_3 or NH_2OH with concentrated sulfuric acid) with ketones in the presence of sulfuric acid. If these component parts:

$$R_2C{=}O, \quad H{-}N{=}, \quad \text{and} \quad H_2SO_4$$

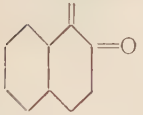
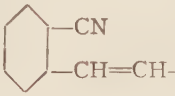
are examined, it will be seen that they may readily interact to produce the sulfate of the oxime, which should, and does, rearrange into the anilide, R—CO—NH—R. Although sulfuric acid is a necessary reagent in this process for the production of the imine residue, it is no doubt also essential for the rearrangement to the anilide.

The sodium salt of benzophenone oxime,[40] $(C_6H_5)_2C{=}NONa$, undergoes a pyrolytic transformation which resembles neither that of the free oxime nor of its hydrochloride. By distilling it in a vacuum of 12 mm., 75.5 percent of the theoretical amount of benzonitrile and 23.3 percent of ammonia escape as volatile products. Since sodium benzamide, $C_6H_5{-}CO{-}NHNa$, also becomes changed into benzonitrile (84.6 percent) and into ammonia (15.4 percent), there may be an interrelationship as Komatsu points out, but more work is needed to establish this with certainty.

[37] Kuhara and Kashima, *Mem. Coll. Sci. Kyoto Imp. Univ.* **4**, 69 (1919); *Chem. Abstracts* **15**, 69 (1921).
[38] Harries and Jablonski, *Ber.* **31**, 1371 (1898).
[39] Schmidt, *Ber.* **57**, 704 (1924).
[40] Komatsu and Hiraidzumi, *Mem. Coll. Sci. Kyoto Imp. Univ.* **8A**, 273 (1925); *Chem. Abstracts* **19**, 2475 (1925).

Other sodium salts of oximes behave as indicated, when they are distilled in a vacuum.

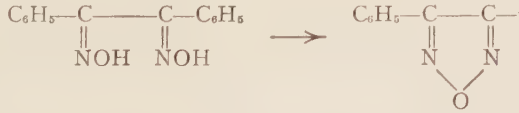
TABLE LIX. *Vacuum Distillation of Sodium Salts of Oximes.*

Sodium Salt of Oxime	Nitrile	Ammonia	Other Products
	Percent		
Acetophenone oxime	14.9 C_6H_5CN	47.8	37.3 benzoic acid; some acetophenone and some acetophenone-oxime
Camphor oxime	96	...	4 of the acid
α-Benzaldoxime $C_6H_5CH{=}NONa.H_2O$	81	7.4	7 benzoic acid; 4.6 benzamide and some benzamidine
*Iso*valeraldoxime $(CH_3)_2CHCH_2CH{=}NONa.H_2O$	97	3	.....
1,2-Naphthoquinone-oxime  , at 250°		...	Referred to in D.R.P. 116, 123; *Chem. Zentr.* 1901, I, 69.

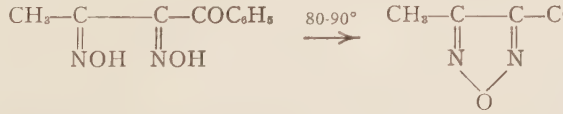
OXIMES OF DIKETONES.

The behavior of benzil monoxime has already been indicated. *Iso*-nitroso-α-hydrindone, $C_6H_4{<}\overset{CH_2}{\underset{CO}{>}}C{=}NOH$, sublimes [41] above 200° and 17 mm., and passes to homophthalimide, $C_6H_4{<}\overset{CH_2}{\underset{CO}{>}}C{=}NH$.

Of the three benzil dioximes, the γ-oxime is the only one [42] to form an anhydride by heating in a vacuum at 155°:

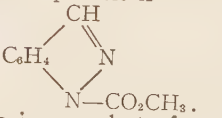


Under similar conditions, the α-oxime is partially isomerized into the β-, and the β- sublimes as such. Similarly, only one of the isomers of methyl-benzoyl-glyoxime [43] forms an anhydride (unless a dehydrating agent such as acetic anhydride is employed):



[41] Peters, *Ber.* **40**, 240 (1907).
[42] Meisenhemier and Lamparter, *Ber.* **57**, 276 (1924).
[43] Ponzio, *Atti accad. sci. Torino*, **57**, 384 (1922); *Chem. Abstracts* **17**, 88.

TABLE LX. *Decomposition of Acetyl Derivatives of Oximes.*

Acyl Derivative of Oximes	Formula	Conditions of Reaction	Substances Formed	Reference
O,N-Diacetyl-*o*-amino-benzaldoxime	—CH=NOAc —NH—Ac	150°; 13 mm.	Acetic acid and *o*-acetyl-aminobenzonitrile	von Auwers and Frese, *Ann.* **450**, 283 (1926).
O,N-Dicarbomethoxy derivative of *o*-amino-benzaldoxime	—CH=NO—CO_2CH_3 —NH—CO_2CH_3	140-150°	Carbon dioxide, methanol and *o*-carbomethoxy-amino-benzonitrile If a trace of calcined soda is present, the exclusive reaction product is  This is a product of re-arrangement	*Ibid.* pp. 274 and 286.
O,N-Dicarbethoxy derivative of *o*-amino-benzaldoxime	Similar	30 minutes at 110-150°; vigorous gas evolution	Carbon dioxide, ethyl alcohol and *o*-carbethoxy-aminobenzonitrile	*Ibid.* p. 287.
O-Carbethoxy-*N*-carbomethoxy derivative of *o*-aminobenzaldoxime	—CH=NO—$CO_2C_2H_5$ —NH—CO_2CH_3	120-130°	*o*-Carbomethoxy-aminobenzonitrile	*Ibid.*
O-Carbethoxy derivative of *o*-benzoylamino-benzaldoxime	—CH=NOCO_2Et —NH—COC_6H_5	Heat	Carbon dioxide, ethyl alcohol and a quantitative yield of *o*-benzoylamino-benzonitrile	*Ibid.* p. 291.

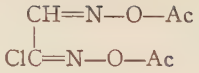
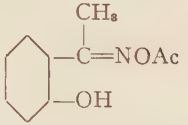
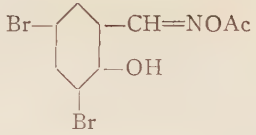
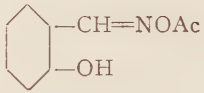
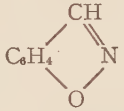
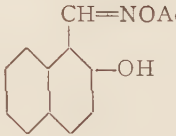
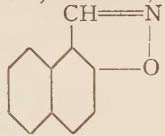
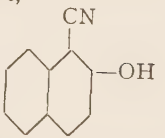
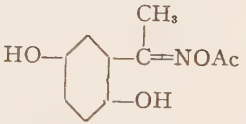
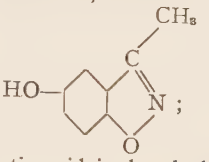
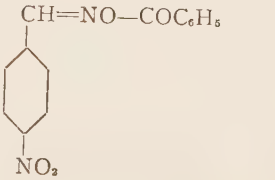
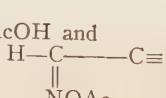
Chloro-*anti*-glyoxime diacetate		200°, at atmospheric pressure	Acetic acid, and a 40 percent yield of chloro-oximido-acetonitrile	Houben and Kaufmann, *Ber.* **46**, 2821 (1913).
2-Hydroxy acetophenone-acetyloxime		160°	2-Methyl indoxazene	Lindemann and Thiele, *Ann.* **449**, 74 (1926).
3-Methyl-6-hydroxy-acetophenone-acetyloxime	Similar	120°	2,4-Dimethyl indoxazene	*Ibid.*
3,5-Dibromosalicyl-aldoxime-monoacetyl derivative		Above melting point, 146°	3,5-Dibromosalicylonitrile	Lindemann and Thiele, *Ann.* **449**, 74 (1926).
2-Hydroxy-benzaldehyde-acetyl-oxime		Slow heating to 130°	Acetic acid and indoxazene, 	*Ibid.*, p. 75.
2-Hydroxy-1-naphth-aldehyde-acetyloxime		Vacuum distillation, 120-135°	Acetic acid is vigorously expelled, giving 4,5(1′,2′-naphthalene)-*iso*xazole, 	Lindemann, Könitzer and Romanoff, *Ann.* **456**, 284 (1927).

TABLE LX. (*Continued*)

Acyl Derivative of Oximes	Formula	Conditions of Reaction	Substances Formed	Reference
2-Hydroxy-1-naphthaldehyde-acetyloxime	Given on p. 665	At somewhat higher temperatures	2-Hydroxy-1-naphthonitrile, 	Lindemann, Könitzer and Romanoff, *Ann.* **456**, 284 (1927).
Quinacetophenone-acetyloxime		160-165° *in vacuo*	4-Hydroxy-2-methyl-indoxazene,  acetic acid is detached at 110°	*Ibid.*
2-Hydroxy-5-methoxy-acetophenone-acetyl-oxime	Similar	160-165° 13 mm.	4-Methoxy-2-methyl-indoxazene.	*Ibid.*
p-Nitrobenzaldehyde-benzoyl-oxime		30 minutes at 140°	Benzoic acid and a quantitative yield of *p*-nitrobenzonitrile	Neber, Hartung and Ruopp, *Ber.* **58**, 1239 (1925).
Diacetate of dioximido-propionic acid		130-140°	CO_2, AcOH and 	Söderbaum, *Ber.* **25**, 908 (1892).

At 240°, the pyrolysis of *iso*nitrosocamphor [44] proceeds with ammonia evolution, yielding camphoric anhydride and dimethyl-heptylenic nitrile, $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(CH_3){-}CN$. More recently, it has been noted that at 206° *iso*nitrosocamphor [45] evolves a gas smelling of ammonia, and that some camphoric α-nitrile is present in the tarry residue. This nitrile may be isolated by steam distillation:

This result is similar to that from α-benzil monoxime, wherein benzonitrile and benzoic acid result from pyrolysis.

Acyl Derivatives of Oximes.

The usual mode of decomposition for the acetyl derivatives of aldoximes is a change into the nitrile, with the detachment of acetic acid. The general reaction is:

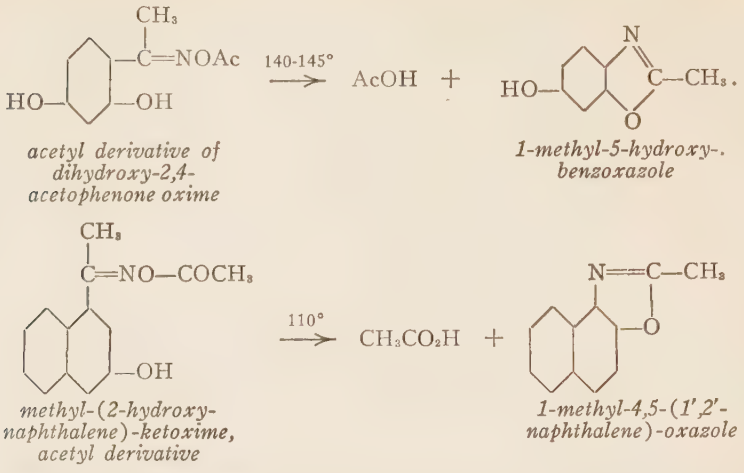
$$R{-}CH{=}N{-}OCOCH_3 \longrightarrow R{-}C{\equiv}N + HO{-}COCH_3.$$

Other acyl groups behave similarly. The examples in Table LX are illustrative.

The data in the table indicate that the acyl-oximes form the nitriles unless an *o*-hydroxy group is present and sometimes if it is present; usually, however, an isomer of the hydroxy-nitrile is formed, namely, an *iso*xazole or indoxazene. In some cases, these latter compounds may be changed into the *o*-hydroxynitriles at a more elevated temperature. This is true with indoxazene-4-azo-1′-(2′-hydroxy-naphthalene), which changes [46] above its melting point, 182°, into 3-cyano-4-hydroxybenzeneazo-1′-(2′-hydroxynaphthalene):

Lindemann has reported two pyrolyses of *o*-hydroxy acetyloximes which apparently give none of the *iso*xazole, but instead give the oxazole, by a process which resembles the Beckmann rearrangement.

[44] Kötz and Wunstorf, *J. prakt. Chem.* **88**, 519 (1913); Tiemann, *Ber.* **33**, 2956 (1900).
[45] Sernagiotto, *Atti accad. Lincei* **26**, II, 221 (1917); *Gazz. chim. ital.* **48**, I, 62 (1918).
[46] Lindemann, Könitzer and Romanoff, *Ann.* **456**, 284, 309 (1927).



acetyl derivative of dihydroxy-2,4-acetophenone oxime

1-methyl-5-hydroxy-. benzoxazole

methyl-(2-hydroxy-naphthalene)-ketoxime, acetyl derivative

1-methyl-4,5-(1',2'-naphthalene)-oxazole

Pyrolysis of the benzenesulfonyl derivatives of dialkyl- or diaryl-ketoximes cause rearrangement. Thus, ten degrees above its melting point (64°), the derivative [47] of dibenzyl-ketoxime, $(C_6H_5CH_2)_2C{=}N{-}O{-}SO_2{-}C_6H_5$, changes into a yellow, viscid mass, which yields benzenesulfonic acid and *N*-benzyl-phenylacetamide, $C_7H_7{-}CONHC_7H_7$, when water is added. A corresponding rearrangement of the benzene sulfonyl derivative of acetone oxime occurs at 130°. Evidence for the rearrangement by heat alone is based on the fact that methyl amine is isolable from the residue if it is merely hydrolyzed with alkalies. Analogously, the *m*-nitrobenzene-sulfonyl derivatives of benzophenoneoxime yields (at the melting point, 24°) benzanilide and *m*-nitrobenzenesulfonic acid (after the addition of water).

Since no purely thermal rearrangement may be induced with acetyl or benzoyl derivatives of dibenzyl ketoxime, one must conclude that in the case of the benzenesulfonyl derivatives, it is the more acidic nature of the acyl group that causes the rearrangement. This reminds one of the fact that the hydrochloride of benzophenoneoxime will rearrange into benzanilide by heating it, whereas the oxime itself fails to do so.

α-Oximino Acids.

Oximino-acetic acid [48] melts at 137°, as it decomposes into carbon dioxide, water and hydrogen cyanide. This transformation also occurs in a sealed tube at 120° with water present:

$$HON{=}CH{-}CO_2H \longrightarrow H_2O + HCN + CO_2.$$

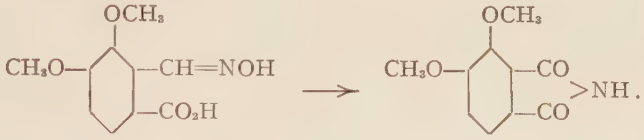
[47] Kuhara and others, *Chem. Abstracts* 13, 119 (1919).
[48] Cramer, *Ber.* 25, 714 (1892).

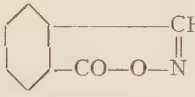
The fact that carbon dioxide is vigorously liberated from α-oximinoglutaric acid at its melting-point, 152°, has been related on p. 416. The oxime of α-ketoadipic acid undergoes pyrolysis [49] into γ-cyanobutyric acid, carbon dioxide and water. The transformation of this type of compound into the nitrile with one less carbon than the original oximino acid is, therefore, quite general. The oxime of phenylglyoxylic acid [50] also behaves in this manner above its melting point:

$$C_6H_5{-}\underset{\underset{NOH}{\|}}{C}{-}CO_2H \longrightarrow C_6H_5CN + CO_2 + H_2O.$$

The oxime [51] of methylcyclohexyl-glyoxylic acid, $(CH_2)_5{=}\underset{\underset{CH_3}{|}}{C}{-}\underset{\underset{NOH}{\|}}{C}{-}CO_2H$, decomposes into the nitrile at 160°.

Heat alone will bring about the Beckmann rearrangement [52] of the oxime of pseudo-opianic acid, with the production of hemipinimide:



The simplest aromatic oximino acid of this type readily forms an anhydride:  , the 6-oxo-derivative of 4,5-benzo-*ortho*-oxazine. This anhydride, if heated suddenly to 120°, rearranges [53] into phthalimide with such an evolution of heat that boiling sets in. With slow heating, *o*-cyanobenzoic acid is isolable as well.

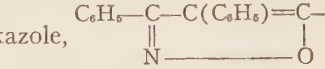
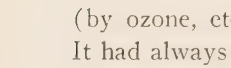
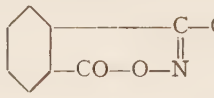
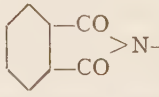
A parallel case [54] is furnished in the following reaction:

$$Br{-}\underset{\underset{Br{-}C{-}CO{-}O}{\|}}{C}{-}\underset{\underset{}{|}}{CH}{=}N \longrightarrow Br{-}\underset{\underset{Br{-}C{-}CO}{\|}}{C}{-}CO \quad >NH.$$

This reaction takes place at the melting point, 125°, of the original compound. A little above that temperature the liquid resolidifies, and at 225° melts again. This is the melting point of the resulting imide.

These rearrangements are of interest because of their bearing on Meisenheimer's hypothesis [55] that in the Beckmann rearrangement of ketoximes, there is an exchange of groups in the *trans* position, and

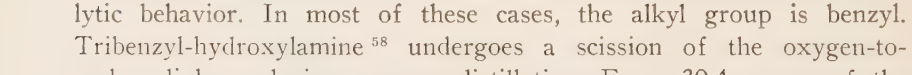
[49] Gault, *Compt. rend.* **148**, 1113 (1909).
[50] Bouveault, *Bull. soc. chim.* [3] **15**, 1018 (1896).
[51] Tarbouriech, *Compt. rend.* **150**, 1606 (1910).
[52] Perkin, Jr., *J. Chem. Soc.* **57**, 1000, 1065 (1890).
[53] Allendorf, *Ber.* **24**, 2347 (1891).
[54] Hill and Cornelison, *Am. Chem. J.* **16**, 299 (1894).
[55] Meisenheimer, *Ber.* **54**, 3206 (1921).

not the *cis* as was assumed in the Hantzsch-Werner theory. These rearrangements of aldoximes behave similarly, and it is of interest to note that Brady [56] has presented other confirmatory evidence for the aldoximes. Meisenheimer reasoned that if an oxime could be converted into a cyclic compound before rearrangement, there would be no doubt as to its spatial configuration (*cis* or *trans*). In his first paper, he described the conversion of triphenyl *iso*xazole,  , (by ozone, etc.) into benzoyl benzil-β-monoxime, melting point 138°. It had always been assumed that the configuration of this oxime derivative was the reverse of that which it was now shown to possess, namely,  . Later, Meisenheimer and Meis [57] presented other similar cases. For example, they showed that in the rearrangement of the following oxime anhydride,  , by concentrated sulfuric acid, there was formed *N*-phenyl-phthalimide,  . Although the last vestige of doubt has not been removed concerning the validity of this method of proof, at least no case is known where the rearrangement proceeds in violation of this mechanism.

Alkyl Hydroxylamines, Amine Oxides, and Nitrones.

Hydroxylamines.

Only a few alkyl hydroxylamines have been studied for their pyrolytic behavior. In most of these cases, the alkyl group is benzyl. Tribenzyl-hydroxylamine [58] undergoes a scission of the oxygen-to-carbon linkage during vacuum distillation. From 30.4 grams of the original substance 8.4 grams of stilbene are produced.



N,N-Dibenzylhydroxylamine may be converted into benzylamine and benzaldehyde, by several hours' boiling in acetic acid. This probably is more than a thermal effect, however.

Benzyl-*iso*nitrosomalonic acid,[59] $C_6H_5CH_2—O—N=C(CO_2H)_2$,

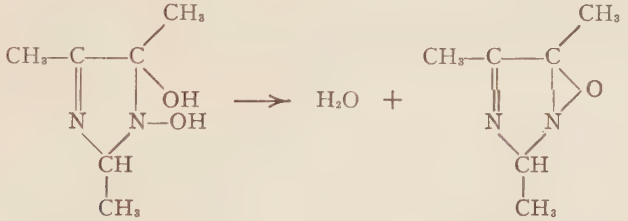
[56] Brady and Bishop, *J. Chem. Soc.* **127**, 1357 (1925).
[57] Meisenheimer and Meis, *Ber.* **57**, 289 (1924).
[58] Kothe, *Ann.* **266**, 319 (1891).
[59] Staudinger and Schneider, *Helv. Chim. Acta* **6**, 316 (1923).

apparently does not yield stilbene when heated, although the substance resembles the previous one by possessing an *O*-benzyl group. Instead, it liberates benzaldehyde and hydrogen cyanide.

O-Benzoyl-*N*,*N*-dibenzyl-hydroxylamine [60] becomes pyrolyzed to benzoic acid in boiling xylene. This transformation may be accomplished more slowly in boiling benzene:

$$C_6H_5CO{-}O{-}N(CH_2C_6H_5)_2 \longrightarrow C_6H_5CO_2H + C_6H_5CH{=}N{-}CH_2C_6H_5.$$

The following substituted imidazole is related to a *N*,*N*-dialkyl hydroxylamine, but as will be seen, its mode of decomposition [61] (by gentle heating) is simply a dehydration between the two hydroxyl groups which are present:



(Melting point, 80°) (Melting point, 134°)

Amine Oxides.

Two types of decomposition appear to be present in the pyrolysis of *amine oxides*. In one, the net effect is the loss of an atom of oxygen, with the production of a tertiary amine: $R_3N{=}O$ into R_3N. Dimethyl-aniline oxide, $\begin{matrix} C_6H_5{-}N(CH_3)_2 \\ \| \\ O \end{matrix}$, behaves in this manner [62] a few degrees above its melting point, 152°, as does *N*-methyl-piperidine oxide, $\begin{matrix} (CH_2)_5N{-}CH_3 \\ \| \\ O \end{matrix}$. Should one of the groups be ethyl [63] or propyl, as in *N*-ethyl-piperidine oxide, this tendency drops to a low value. Some ethyl piperidine is formed, but for the most part, ethylene is energetically eliminated (142°) and cyclopentamethylene-hydroxylamine is formed:

$$(C_5H_{10}){=}\underset{\underset{O}{\|}}{N}{-}C_2H_5 \longrightarrow (C_5H_{10}){=}N{-}OH + C_2H_4.$$

[60] Gambarjan and Cialtician, *Ber.* **60**, 390 (1927).
[61] Diels, *Ber.* **51**, 965 (1918).
[62] Bamberger and others, *Ber.* **32**, 246, 1890 (1899); **34**, 1082 (1901).
[63] Wernick and Wolffenstein, *Ber.* **31**, 1560 (1898); Michael, *J. Am. Chem. Soc.* **43**, 330 (1921).

Tripropylamine oxide decomposes smoothly [64] in this manner by heating in a vacuum:

$$(C_3H_7)_3N{=}O \longrightarrow (C_3H_7)_2N{-}OH + C_3H_6.$$

Bewad [65] has reported the facile decomposition of diethyl-alkoxy-ammonium hydroxide into *N,N*-diethylhydroxylamine:

$$C_2H_5{-}\overset{\displaystyle OR}{\underset{\displaystyle C_2H_5}{N}}H{-}OH \longrightarrow ROH + (C_2H_5)_2N{-}OH.$$

Meisenheimer has established the identity [66] of two isomeric compounds of the formula: $\begin{matrix}(CH_3)_3N{-}OH\\ |\\ OCH_3\end{matrix}$. Their fundamental difference is revealed in their decompositions in solution when heated. Trimethyl-methoxy-ammonium hydroxide changes quantitatively into trimethyl amine and formaldehyde:

$$(CH_3)_3N{<}\begin{matrix}OCH_3\\ OH\end{matrix} \longrightarrow (CH_3)_3N + CH_2O + H_2O,$$

whereas trimethylhydroxyammonium methylate, under similar circumstances, yields the amine oxide and methanol:

$$(CH_3)_3N{<}\begin{matrix}OH\\ OCH_3\end{matrix} \longrightarrow (CH_3)_3N{=}O + CH_3OH.$$

In interpretation of these phenomena, Jones [67] has designated these isomers "electromers", and has provided an explanation for the first reaction on the basis of the formula $(CH_3)_3N{<}\begin{matrix}\times OCH_3\\ \times OH\end{matrix}$; and the second, on the formula $(CH_3)_3N{<}\begin{matrix}\times OH\\ \times OCH_3\end{matrix}$. In more modern terminology, this idea may be expressed in the equations:

$$\left(\begin{matrix}&Me&&H&\\ Me:&\ddot{N}&:\ddot{O}:&\ddot{C}&:H\\ &Me&&H&\end{matrix}\right)^{+} \quad :\ddot{O}:H^{-} \longrightarrow \begin{matrix}&Me&&&H&\\ Me:&\ddot{N}&:&\ddot{O}::&\ddot{C}&:H\\ &Me&&&&\end{matrix} + H:\ddot{O}:H.$$

and

$$\left(\begin{matrix}&Me&&\\ Me:&\ddot{N}&:\ddot{O}:&H\\ &Me&&\end{matrix}\right)^{+} \quad :\ddot{O}:CH_3^{-} \longrightarrow \begin{matrix}&Me&&\\ Me:&\ddot{N}&:\ddot{O}:&\\ &Me&&\end{matrix} + H:\ddot{O}:CH_3.$$

[64] Mamlock and Wolffenstein, *Ber.* **33**, 161 (1900).
[65] Bewad, *J. prakt. Chem.* [2] **63**, 94 (1901).
[66] Meisenheimer, *Ann.* **397**, 273 (1913); **385**, 117 (1911); **396**, 75 (1913); **399**, 371 (1913).
[67] Jones, *J. Am. Chem. Soc.* **36**, 1286 (1914).

NITRONES.

Nitrones have the structure, $-C(=O)-N=R$. Phenyl-*N*-phenyl nitrone undergoes a partial rearrangement [68] above its melting point, 112°, into benzanilide:

$$C_6H_5-CH=N(=O)-C_6H_5 \longrightarrow C_6H_5CONHC_6H_5.$$

In addition, there are indications of the following reactions:

$$2C_6H_5CH=N(=O)-C_6H_5 \longrightarrow 2C_6H_5CHO + C_6H_5-N=N-C_6H_5$$

$$2C_6H_5CH=N(=O)-C_6H_5 \longrightarrow 2C_6H_5CH=N-C_6H_5 + 2[O]$$

$$2C_6H_5CH=N(=O)-C_6H_5 \longrightarrow 2C_6H_5NO + C_6H_5CH=CHC_6H_5 \text{ (not identified)}$$

The anilides are also formed when *p*-anisyl-*N*-phenyl nitrone and *o*-hydroxyphenyl-*N*-phenyl nitrone are heated. Alessandri's technic consists merely in melting the nitrone in an open test-tube. On cooling, crystals of the anilides separate from the oily residue.

The trisubstituted nitrones, in other words those which are related to ketones just as the preceding ones have been to aldehydes, possess no mobile hydrogen to produce anilides. However, if triphenyl nitrone, $(C_6H_5)_2C(=O)N-C_6H_5$, is heated (in benzene) for five hours [69] at 250°, benzophenone and benzophenone-anil, $(C_6H_5)_2C=NC_6H_5$, are formed, and no gaseous products. If the nitrone is heated directly, the odor of nitrosobenzene may be recognized.

Diphenylene-*N*-phenyl nitrone, $C_6H_4(C_6H_4)>C=N(=O)-C_6H_5$, yields fluorenone [70] and aniline, by heating in benzene solution at 250°.

HYDROXAMIC ACIDS AND THE LOSSEN REARRANGEMENT.

MONOHYDROXAMIC ACIDS.

Mono-, di- and tri-hydroxamic acids are known, and the terminology indicates one, two and three acyl groups attached to the hydroxylamine

[68] Staudinger and Miescher, *Helv. Chim. Acta* **2**, 563 (1919); Alessandri, *Gazz. chim. ital.* **51**, I, 75 (1921).
[69] Staudinger and Miescher, *Helv. Chim. Acta* **2**, 569 (1919).
[70] *Ibid.* p. 554.

nucleus. The most interesting reaction of these compounds is their rearrangement, originally discovered by Lossen,[71] wherein a radical wanders from carbon to nitrogen. The customary procedure is to heat the salt of a dihydroxamic acid, either in aqueous solution:

$$R{-}CO{-}N\langle^{Na}_{O{-}CO{-}R} \longrightarrow [R{-}CO{-}N{=}] + NaO{-}CO{-}R$$

$$[R{-}CO{-}N{=}] \longrightarrow R{-}N{=}C{=}O \quad (\textit{isocyanate})$$

$$R{-}N{=}C{=}O \xrightarrow{H_2O} CO_2 + RNH_2, \text{ or } (RNH)_2CO \quad (\textit{amine}, \textit{urea})$$

or to heat the salt[72] by itself:

$$(C_6H_5)_2CH{-}CO{-}N\langle^{Ag}_{O{-}COCH_3} \xrightarrow{110^\circ} CH_3CO_2Ag + (C_6H_5)_2CH{-}NCO.$$

$$C_6H_5CO{-}NK{-}O{-}CO{-}C_4H_3S \xrightarrow{140^\circ} C_4H_3S{-}CO_2K + C_6H_5{-}NCO.$$

$$C_4H_3S{-}CO{-}N\langle^{Na}_{O{-}CO{-}C_6H_5} \xrightarrow{160^\circ} C_6H_5CO_2Na + C_4H_3S{-}NCO.$$

In the dry state, many of these salts have a fairly definite temperature at which decomposition occurs. In a few cases, as with the potassium salt of the benzoyl ester of phenylacethydroxamic acid,[73] it is spontaneous and rather violent.

As would be expected, it has been found possible to construct an electron-attraction series for the various radicals R, in R—CO—NHOH, depending on the relative ease of rearrangement into R—NCO. This has been systematically attempted, however, only in a few cases. Thus the series of Jones and Hurd, methyl > benzyl > benzohydryl > triphenylmethyl, is in perfect agreement with the same series obtained by other methods (see p. 28). Methyl, being more firmly attached to the carbonyl group in acethydroxamic acid than is triphenylmethyl in triphenylacethydroxamic acid, is less prone to undergo rearrangement than triphenylmethyl. Similarly, there is the series:[74] cyclopropyl > benzylmethyl > *iso*propyl > dibenzylmethyl. Scott[75] has also obtained results which seem to indicate the following series: methyl > ethyl >

[71] Lossen, *Ann.* **161**, 359 (1872); **175**, 271 (1875); **186**, 1 (1876); **252**, 170 (1889).
[72] Jones and Hurd, *J. Am. Chem. Soc.* **43**, 2437, 2447, 2445 (1921).
[73] Jones, *Am. Chem. J.*, **48**, 6 (1912).
[74] Jones and Scott, *J. Am. Chem. Soc.* **44**, 411 (1922).
[75] Scott, *Science* **59**, 583 (1924).

*iso*propyl > phenyl. In this latter series, phenyl seems out of place (see pp. 28, 38), but the other three radicals coincide in position with the results of other methods.

The potassium salt[76] of benzoyl methoxyacethydroxamic acid, $CH_3O—CH_2—CO—NK—OCOC_6H_5$, rearranges at 100° to methoxymethyl *iso*cyanate, $CH_3O—CH_2—NCO$, an oil which polymerizes in the course of a few days into a vitreous solid. In a strictly analogous manner, methoxy-ethyl *iso*cyanate is prepared from the corresponding derivative of β-methoxy-propionhydroxamic acid. The potassium salt of benzoyl α-benzylpropionhydroxamic acid has been observed to decompose spontaneously[77] at room temperature. This rearrangement to the *iso*cyanate also occurs in cold water, but hot water reacts with the *iso*cyanate to produce the urea.

$$C_6H_5CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CO—NK—O—COC_6H_5 \longrightarrow C_6H_5CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—NCO + C_6H_5CO_2K$$

The potassium salt of diacethydroxamic acid,[78] $CH_3CO—NK—O—COCH_3$, also decomposes by heating into potassium acetate and methyl *iso*cyanate, but in the presence of water the *iso*cyanate yields dimethyl urea.

If the formula of the monohydroxamic acid is examined, it will be noticed that it is necessary only to detach a molecule of water to induce rearrangement. Thus,

$$R—CO—N\langle\begin{matrix}H\\OH\end{matrix} \longrightarrow [R—CO—N=] + H_2O \longrightarrow R—N=C=O,$$

or the amine or urea. It has frequently been noted that this transformation occurs by pyrolysis, but with the simplest member, namely, formohydroxamic acid, this does not occur. Instead,[79] above 80° the compound dissociates violently into carbon monoxide and hydroxylamine:

$$H—CO—NHOH \longrightarrow CO + NH_2OH.$$

Formyl chloride oxime, $Cl—CH=NOH$, undergoes pyrolysis[80] into hydrogen chloride and fulminic acid. Hydroxylamine is eliminated from phenylhydroxyurea without any accompanying rearrangement.[81] This has been expounded on p. 612.

[76] Jones and Powers, *J. Am. Chem. Soc.* **46**, 2518 (1924).
[77] Jones and Wallis, *ibid.* **48**, 172 (1926).
[78] Thiele and Pickard, *Ann.* **309**, 203 (1900).
[79] Jones, *Am. Chem. J.* **20**, 28 (1898); Jones and Oesper, *ibid.* **42**, 517 (1909).
[80] Biddle, *Ann.* **310**, 13 (1899); *Ber.* **38**, 3858 (1905).
[81] Hurd, *J. Am. Chem. Soc.* **45**, 1483 (1923).

The rearrangement of monohydroxamic acids, Ar—CO—NHOH, by heat was early studied by Lossen. Distillation of benzohydroxamic acid, for example, was found [82] to yield carbon dioxide and aniline, but in no sense should the reaction be construed in the sense of the simple statement: $C_6H_5CONHOH$ into $C_6H_5NH_2 + CO_2$. From 3 grams of the hydroxamic acid, only 0.45 gram of an impure aniline *hydrochloride* was obtained. Anishydroxamic acid and *p*-toluylhydroxamic acid behaved similarly. In all three cases, Lossen found that a rather smooth conversion to the aromatic amines could be realized by dry-distilling the barium salts of the respective hydroxamic acids.

Jones and Root have recently investigated [83] the behavior of *o*-benzohydryl-benzohydroxamic acid. Two degrees above the melting point, 178°, it rearranges to the urea; one gram leaves 0.6 gram of the residual urea:

$$2(C_6H_5)_2CH—C_6H_4—CO—NHOH \longrightarrow (C_6H_5)_2CH—C_6H_4—NH)_2CO + CO_2 + H_2O$$

This is a perfectly normal rearrangement, and there is apparently no tendency to form diphenyl-phthalimidine, $C_6H_4<\begin{matrix}C(C_6H_5)_2\\ CO\end{matrix}>NH$ by loss of water. It is interesting to note that the hydroxamic acid is isomeric with triphenylacethydroxamic acid; however, the ease of its rearrangement is more comparable to that of benzohydroxamic acid, H—C_6H_4—CO—NHOH, with which it is structurally related, than with triphenylacethydroxamic acid, with which it is isomeric. This may be interpreted to mean that the electron attraction of the *o*-benzohydrylphenyl radical is comparable to that of phenyl, and far different from that of triphenylmethyl. This is a very reasonable behavior.

Dichloroacethydroxamic acid may be prepared [84] by the interaction of ethyl dichloroacetate and hydroxylamine base at −10°. The substance melts at 86°, and undergoes pyrolysis in 10 minutes at 110-145° in a hydrogen atmosphere to give the following isolated products: carbon dioxide, hydrogen cyanide, hydrogen chloride, dichloroacetic acid, dichloroacetamide and ammonia. The following reactions are presented to explain this behavior:

$$CHCl_2—CO—NHOH \longrightarrow [CHCl_2—NCO + H_2O] \longrightarrow [CHCl_2—NH_2] + CO_2$$

$$\downarrow$$

$$HNC + 2HCl$$

[82] Lossen, *Ann.* 175, 320 (1875).
[83] Jones and Root, *J. Am. Chem. Soc.* 48, 191 (1926).
[84] Jones and Sneed, *J. Am. Chem. Soc.* 39, 668 (1917).

and a series of secondary reactions:

$$CHCl_2—CO—NHOH + H_2O \longrightarrow CHCl_2—CO_2H + [NH_2OH]$$
$$2CHCl_2—CO—OH + HNC \longrightarrow [(CHCl_2—CO)_2O + H—CONH_2]$$

Thus:

$$CHCl_2—CO—OH + HNC \xrightarrow{H_2O} CHCl_2—CONH_2 + [H—CO_2H]$$
$$[HCO_2H] + [NH_2OH] \longrightarrow CO_2 + NH_3 + H_2O.$$

Benzoyl-formohydroxamic acid pyrolyzes quantitatively into benzamide and carbon dioxide at the melting point:

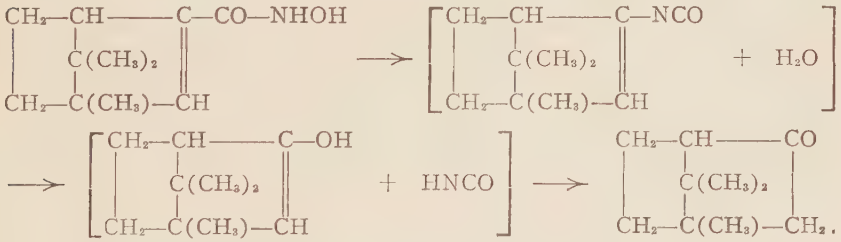
$$C_6H_5CO—CO—NHOH \longrightarrow C_6H_5CONH_2 + CO_2.$$

Very probably the mechanism in this case [85] is similar to the preceding ones:

$$R—CO—CONHOH \longrightarrow [H_2O + R—CO—NCO] \longrightarrow R—CONH_2 + CO_2.$$

p-Bromobenzoyl-formohydroxamic acid [86] behaves analogously (at melting point, 141°), and yields *p*-bromobenzamide.

Bornylene-3-hydroxamic acid undergoes pyrolysis at its melting point. The rearrangement product [87] would be an α-unsaturated *iso*-cyanate, but this hydrolyzes, with evolution of ammonia, into epi-camphor:

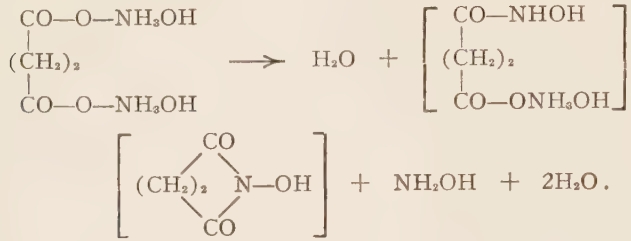


Bornylene-2-hydroxamic acid [88] decomposes at 120°, whereupon the temperature at once advances to 200° with the evolution of ammonia and the formation of camphor.

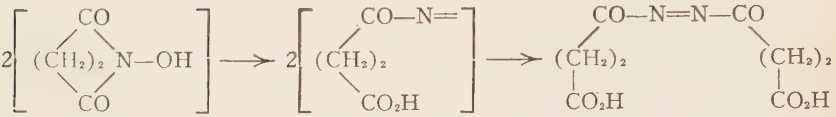
Some hydroxylammonium salts change into the hydroxamic acids by heating. Hydroxylammonium succinate (p. 512) does not, but if the pyrolysis proceeds through the hydroxamic acid, as it possibly does, the mode of decomposition from that point on differs from the simple hydroxamic acids. Very possibly, it proceeds through a "succinamide

[85] Gastaldi, *Gazz. chim. ital.* 54, 582 (1924).
[86] Gastaldi and Principalle, *ibid.* 56, 557 (1926).
[87] Bredt and Perkin, *J. prakt. Chem.* 197, 232 (1914).
[88] Bredt and Perkin, *ibid.* p. 252.

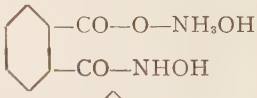
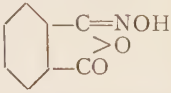
to succinimide" type of pyrolysis which would account for the non-rearrangement to an *iso*cyanate. Thus:



Then



Pyrolysis of the hydroxylamine would supply the requisite ammonia for the mono-ammonium salt of the compound, $(=N—CO(CH_2)_2CO_2H)_2$, which was actually isolated. This is the only case in which the univalent nitrogen derivative, (R—CO—N=), couples with itself instead of undergoing rearrangement into an *iso*cyanate.

Hydroxylammonium phthalylhydroxamate,  , decomposes[89] at 130° into phthalyl hydroxylamine,  , hydroxylamine and water; a secondary reaction gives rise to ammonium phthalyl-hydroxamate.

Dihydroxamic Acids.

Dibenzohydroxamic acid yields phenyl *iso*cyanate by distillation:

From 86 grams originally, Pieschel[90] identified 24.4 grams of phenyl *iso*cyanate, 27.5 grams of benzoic acid, 4.5 grams of carbon dioxide, and 20.1 grams of benzanilide. The last may be explained as a reaction product of phenyl *iso*cyanate and benzoic acid, or possibly it is formed by simple loss of carbon dioxide from the original dihydroxamic acid

[89] Errera, *Gazz. chim. ital.* **24**, II, 469 (1894).
[90] Pieschel, *Ann.* **175**, 311 (1875).

Pieschel also studied the pyrolysis of benzanishydroxamic acid, and it also appeared to follow the two equations:

$$C_6H_5—CO—N<\begin{matrix}H\\ O—CO—C_6H_4OCH_3\end{matrix} \begin{matrix}\nearrow\ C_6H_5NCO + HO_2C—C_6H_4OCH_3\\ \searrow\ CO_2 + C_6H_5—CO—NH—C_6H_4OCH_3.\end{matrix}$$

Similarly, with anisbenzohydroxamic acid:

$$CH_3OC_6H_4—CO—N<\begin{matrix}H\\ O—CO—C_6H_5\end{matrix} \begin{matrix}\nearrow\ CH_3O—C_6H_4—NCO + C_6H_5CO_2H\\ \searrow\ CO_2 + CH_3OC_6H_4—CO—NHC_6H_5.\end{matrix}$$

The *O*-ethyl ether of dibenzohydroxamic acid [91] pyrolyzes into acetaldehyde at about 170-185°, but gives no *iso*cyanate:

$$C_6H_5—\overset{OC_2H_5}{\overset{|}{C}}=N—O—COC_6H_5 \longrightarrow CH_3CHO + C_6H_5CO_2H + C_6H_5CN,$$

and some phenyl *iso*cyanide. The acetyl derivative of benzohydroxamic acid is quite a stable compound, but strong heating [92] breaks it up into phenyl *iso*cyanate:

$$C_6H_5CO—NH—OCOCH_3 \longrightarrow C_6H_5—NCO + CH_3CO_2H.$$

The benzoyl ester of dichloroacethydroxamic acid, $CHCl_2—CO—NH—OCOC_6H_5$, if heated at 150° in a hydrogen atmosphere, changes [84] into dichloromethyl-*iso*cyanate, $CHCl_2—NCO$. Rearrangement of a somewhat different type comes by heating the benzoyl ester of lacthydroxamic acid. The *α*-hydroxyl group is the responsible feature, since the corresponding derivative of mandelic acid behaves similarly. The equations suggested by Jones and Neuffer [93] to explain the formation of acetaldehyde and *symmetrical* dibenzoyl urea in the former case, indicate a cleavage plane, not at $CH_3—CHOH—CO—N<\begin{matrix}H\\ OCOC_6H_5\end{matrix}$, but at

$$CH_3—\overset{OH}{\overset{|}{C}}HOH—\overset{|}{C}=N—OCOC_6H_5:$$

$$CH_3—CHOH—C(OH)=NOCOC_6H_5 \longrightarrow CH_3CHO + H_2O + [C=N—O—CO—C_6H_5] \longrightarrow O=C=N—COC_6H_5$$

$$H_2O + O=C=N—COC_6H_5 \longrightarrow C_6H_5CONH_2 + CO_2$$

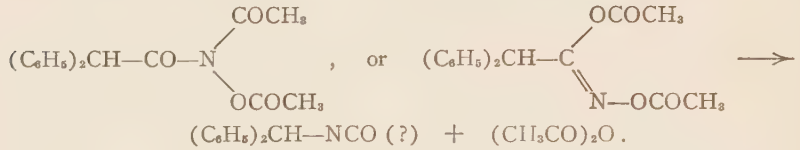
and later,

$$C_6H_5CO—NCO + C_6H_5CONH_2 \longrightarrow CO(NH—COC_6H_5)_2.$$

Thermal decomposition of the benzoyl ester of diphenylacethydroxamic acid,[94] $(C_6H_5)_2CH—CO—NH—O—COC_6H_5$, gives vapors which

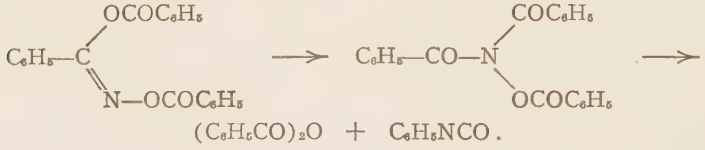
[91] Gürke, *Ann.* **205**, 280, 285 (1880).
[92] Hantzsch, *Ber.* **27**, 1256 (1894).
[93] Jones and Neuffer, *J. Am. Chem. Soc.* **39**, 659 (1917).
[94] Jones and Hurd, *J. Am. Chem. Soc.* **43**, 2434 (1921).

possess an *iso*cyanate odor (probably diphenylmethyl *iso*cyanate). This *iso*cyanate may also have been formed during the dry distillation of the diacetyl derivative of the same acid, but acetic anhydride is the only product which has been definitely identified. The yield is about 0.5 gram from 2 grams:



Trihydroxamic Acids.

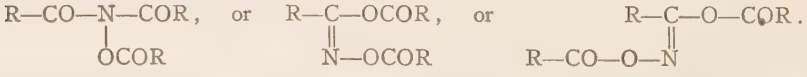
Tribenzohydroxamic acid [95] completely changes into phenyl *iso*cyanate and benzoic anhydride by dry distillation:



The exact structure of trihydroxamic acids is debatable. It is known that the first acyl group to become attached to the hydroxylamine nucleus is bound to nitrogen, and the second to the hydroxylamine-oxygen:

Mono-hydroxamic acids: R—CO—NHOH
(or R—C(OH)=NOH)
Di-hydroxamic acids: R—CO—NH—OCOR
(or R—C(OH)=NOCOR).

The trihydroxamic acids, therefore, must be either



Actually, three tribenzohydroxamic acids are known. In more complex trihydroxamic acids, it is difficult to account for all the facts of pyrolysis without arbitrary assumptions. However, as the following cases will show, it is the *first* acyl group of the three to be attached to the hydroxylamine nucleus that is largely detached as an *iso*cyanate by heating:

[95] Steiner, *Ann.* **178**, 225 (1875); Lossen, *Ann.* **281**, 273 (1894).

wherein v and v′ represent the third and second acyl radicals.

Lossen prepared the triacyl-hydroxylamines:

Benzanisbenzhydroxylamine, $C_6H_5-C(=N-O-anisoyl)(O-benzoyl)$

Dibenzanishydroxylamine, $C_6H_5-C(=N-O-benzoyl)(O-anisoyl)$

Anisdibenzhydroxylamine, $CH_3O-C_6H_4-C(=N-O-benzoyl)(O-benzoyl)$

He showed that the first two pyrolyze very largely (90 percent) into phenyl *iso*cyanate and benzoic anisic anhydride, (benzoyl-*O*-anisoyl), and only about 10 percent into *p*-methoxyphenyl *iso*cyanate and benzoic anhydride. The third isomer, however, was found to yield about 75 percent of *p*-methoxyphenyl *iso*cyanate and benzoic anhydride, and only 25 percent of the alternative products. These two types of pyrolysis for the three compounds [96] may be represented as follows:

$$N\begin{Bmatrix}COC_6H_5\\COC_6H_5\\COC_6H_4OCH_3\end{Bmatrix}O \swarrow \begin{matrix}C_6H_5NCO + C_6H_5CO-O-COC_6H_4OCH_3\\CH_3OC_6H_4NCO + (C_6H_5CO)_2O\end{matrix}$$

Jones [97] has discussed these reactions critically.

The di-phenylcarbamyl ester of benzohydroxamic acid [98] melts at 113°; it resolidifies at 125°, and at 145° it liberates carbon dioxide. *Symmetrical*-diphenylurea is formed, and also presumably phenyl *iso*cyanate. No search for the latter was made:

$$C_6H_5CO-N<\begin{matrix}CONH-C_6H_5\\O-CONHC_6H_5\end{matrix} \longrightarrow$$

$$[C_6H_5-CO-N=] + \left[O<\begin{matrix}CO-NHC_6H_5\\CO-NHC_6H_5\end{matrix}\right]$$

$$\downarrow \qquad\qquad \downarrow$$

$$C_6H_5-N=C=O \qquad CO_2 + CO(NHC_6H_5)_2.$$

THIOHYDROXAMIC ACIDS.

They behave differently from the hydroxamic acids when they are heated. Instead of rearranging to an *iso*thiocyanate, sulfur is detached

[96] Lossen, *Ann.* **186**, 18, 25, 26, 44 (1877).
[97] Jones, *Am. Chem. J.*, **48**, 22 (1912).
[98] Hurd, *J. Am. Chem. Soc.* **45**, 1485 (1923).

and a nitrile is formed. Thus, benzothiohydroxamic acid [99] gives rise to benzonitrile:

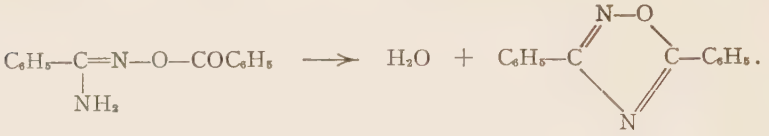
$$C_6H_5—CS—NHOH \longrightarrow C_6H_5CN + S + H_2O.$$

and phenyl thiohydroxyurea [100] yields cyananilide:

$$C_6H_5NH—CS—NHOH \text{ (or } C_6H_5N{=}C(SH)—NHOH) \longrightarrow C_6H_5NH—CN \text{ (or } C_6H_5N{=}C{=}NH) + S + H_2O.$$

In the latter case, the breakdown occurs even in boiling alcohol solution.

The action of heat on benzoyl-benzenylamidoxime [101] is to cause dehydration with the formation of dibenzenylazoxime:



Bromoamides and the Hofmann Rearrangement.

The sodium salts of bromoamides yield *iso*cyanates by heating, and the principle of the change is no different from the Lossen rearrangement.

$$R—CO—N\langle^{Na}_{Br} \longrightarrow NaBr + [R—CO—N{=}] \longrightarrow R—N{=}C{=}O.$$

Usually this reaction [102] is performed in solution, in which case the *iso*cyanate reacts with the solvent (water or alcohol). The bromoamides are more stable than their salts. However, dibromosalicylic bromoamide undergoes rearrangement [103] even at −12°.

Iodine is liberated rather easily by heating iodoacetamide,[104] CH_3CONHI.

Acid-azides and the Curtius Rearrangement.

Most acid azides rearrange so readily by heating that it is customary to perform the pyrolysis in a solvent. If the *iso*cyanate is desired, benzene is quite frequently used. The general reaction is:

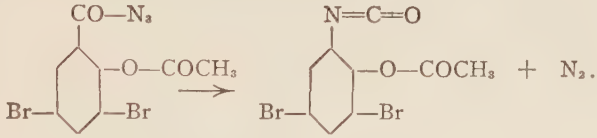
$$R—CO—N{=}N{\equiv}N \longrightarrow N_2 + [R—CO—N{=}] \longrightarrow R—N{=}C{=}O.$$

Only a few cases will be selected to illustrate this reaction.

[99] Cambi, *Atti. accad. Lincei* **18**, I, 687 (1909).
[100] Tiemann, *Ber.* **22**, 1939 (1889).
[101] Tiemann and Krueger, *Ber.* **17**, 1694 (1884).
[102] Hofmann, *Ber.* **15**, 756 (1882); Maugin, *Ann. chim.* [8] **22**, 316 (1911).
[103] McCoy and Stieglitz, *Am. Chem. J.* **21**, 116 (1899); Van Dam, *Rec. trav. chim.* **18**, 408 (1899); **19**, 318 (1900).
[104] Seliwanow, *Ber.* **26**, 987 (1893).

The transformation of benzazide into phenyl *iso*cyanate by heating in benzene is a well known reaction. To prevent a possible explosion, Wieland has recently suggested [105] that the solvent benzene be removed at atmospheric pressure, before the ultimate distillation at reduced pressure. Crude benzazide explodes [106] in the temperature range of 120-165°, but deflagrates at lower or higher temperatures. On the other hand, pure benzazide merely deflagrates between 90-230°.

2,4,6-Tribromobenzazide, $[C_6H_2Br_3—CON_3]$, rearranges [107] as it is formed, even at 0°, as does 2,5-dibromobenzazide and 2,6-dibromo-4-methyl-benzazide. 2-Acetoxy-3,5-dibromo-benzazide [108] changes into 2-acetoxy-3,5-dibromo-phenyl*iso*cyanate by heating it in benzene solution:



Either the *cis* or the *trans* forms of cinnamic acid azide,[109] $C_6H_5CH=CH—CON_3$, change into the *trans* form of styryl *iso*cyanate (yield, 3 grams from 5 grams) on heating in benzene solution. The azide of crotonic acid, $CH_3CH=CH—CON_3$, gives off nitrogen rapidly at 75-85° (no solvent) and gives *iso*allyl *iso*cyanate. Curtius has observed that in boiling benzene, *p*-bromohippurazide [110] yields *p*-bromohippenyl *iso*cyanate as nitrogen is liberated. Much of Curtius' work has dealt with the reactions of azides of the most varying types.

The azide related to 2-hydroxy-3-naphthoic acid [111] melts at 133° and explodes at higher temperatures. When heated in benzene, it gives a 90 percent yield of the *iso*cyanate:

α-Benzyl-propionazide [112] decomposes unimolecularly in benzene at 35°, giving a 97 percent yield of the *iso*cyanate. Some nitrogen is evolved even at 10°. Since the *dextro*-azide yields the *dextro-iso*cyanate, this

[105] Wieland, *Z. angew. Chem.* **39**, 900 (1926).
[106] Bergel, *ibid.* **40**, 974 (1927).
[107] Buning, *Rec. trav. chim.* **40**, 327 (1921).
[108] Lindemann and Schultheis, *Ann.* **451**, 241 (1927).
[109] Jones and Mason, *J. Am. Chem. Soc.* **49**, 2528 (1927).
[110] Curtius, *J. prakt. Chem.* **87**, 513 (1913).
[111] Fries, *Ber.* **58**, 2845 (1925).
[112] Jones and Wallis, *J. Am. Chem. Soc.* **48**, 172 (1926).

experiment demonstrates that racemization does not occur during rearrangement:

$$C_6H_5CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CON_3 \longrightarrow N_2 + C_6H_5CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}NCO.$$

Disubstituted carbamazides have been discussed on page 612, and there it was pointed out that they undergo the normal Curtius rearrangement whereas the monosubstituted carbamazides fail to rearrange. Stollé's method [113] consists in heating the carbamazide either in boiling xylene or in tetralin at 160-190°; the former solvent is employed for diaryl carbamazides, $Ar_2N{-}CO{-}N_3$, and the duration of heating varies from 30 minutes to 10 hours. Nitrogen is usually evolved in nearly quantitative amounts, but instead of getting the *iso*cyanate derivative, $Ar_2N{-}NCO$, an indazolone is invariably formed, due, no doubt, to further reaction of the *iso*cyanate. In general,

$$X{-}C_6H_4{-}\underset{\displaystyle R}{\underset{|}{N}}{-}CO{-}N_3 \longrightarrow N_2 + X{-}C_6H_3\!<\!\begin{matrix}CO\\ N\\ R\end{matrix}\!>\!NH.$$

Stollé has found this to be the case when

C_6H_4 X represents	and R represents
p-tolyl	ethyl.
p-tolyl	*p*-tolyl.
phenyl	benzyl.
α-naphthyl	phenyl.
β-naphthyl	phenyl.
β-naphthyl	β-naphthyl.

Either hot xylene or hot tetralin may be utilized to effect the rearrangement of dialkyl carbamazides, $R_2N{-}CO{-}N_3$; R_2 represents dimethyl, di*iso*butyl or di*iso*pentyl. The residual material, after the nitrogen has been detached, is not the simple *iso*cyanate, $R_2N{-}NCO$, but a derivative of it; for example, the substance from di*iso*pentyl-carbamazide is $C_{22}H_{47}O_2N_5$, which may be a "biuret" derivative, $NH(CO{-}NH{-}N(C_5H_{11})_2)_2$.

In spite of the fact that solutions of aromatic sulfonazides liberate nitrogen by heating, rearrangement is never [114] encountered. Instead, the residue, $[R{-}SO_2{-}N{=}]$, reacts with the solvent. For example, in hot toluene solution, benzenesulfonazide liberates nitrogen and forms the benzenesulfonyl derivative [115] of *o*-toluidine, $C_6H_5SO_2NH{-}C_6H_4CH_3$.

A convenient synthesis of *iso*cyanates [116] is to heat acid chlorides in

[113] Stollé, *Ber.* **57**, 1063 (1924); *J. prakt. Chem.* **117**, 185 (1927).
[114] Curtius, *Chem. Ztg.* **37**, 214 (1913); *J. prakt. Chem.* **112**, 65, 88 (1926).
[115] Bertho, *Ber.* **57**, 1138 (1924).
[116] Schroeter, *Ber.* **42**, 3357 (1909).

an inert solvent (amyl ether) with sodium azide. From 15.5 grams of acetyl chloride and 14.5 grams of sodium azide, 10 grams of the isocyanate is formed.

$$CH_3COCl + NaN_3 \longrightarrow CH_3NCO + N_2 + NaCl.$$

Obviously, the azide is the intermediate product in this case.

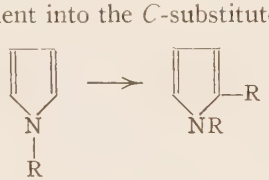
CHAPTER 23.

N-HETEROCYCLIC COMPOUNDS.

The formation of pyrrole, indole, quinoline and related compounds by pyrogenic methods from certain proteins has been mentioned on pages 465-7. Only the pyrolysis of the *N*-heterocyclic compounds will be treated in this chapter. The pyrolysis of *N*-heterocyclic acids has been given in Chapters 13, 14 and 15, and chiefly on pages 372-391, 395, 399, 411-2, 418, 422-3. Almost the universal reaction is one of decarboxylation.

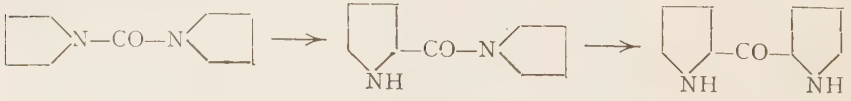
N-Heterocyclic Compounds with Only One Nitrogen Per Nucleus.

One of the characteristic pyrogenic reactions of *N*-substituted pyrroles is a rearrangement into the *C*-substituted isomers. Thus:



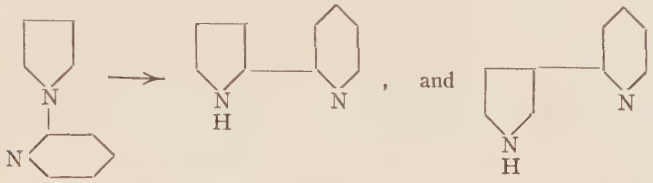
(R = alkyl, aryl or acyl)

As an example of such a conversion, *N*-methyl pyrrole [1] changes into *α*-methyl pyrrole by passage through a tube heated to dull redness. A secondary reaction leads to the formation of appreciable quantities of pyridine. There is neither gas nor charring. By the same kind of treatment, two-thirds of *N*-phenyl pyrrole [2] may be recovered as such, but one-third is transformed into *α*-phenyl pyrrole. At dull red heat, *N*-benzoyl pyrrole [3] (boiling point 276°) rearranges into *α*-benzoyl pyrrole; and between 250-280°, *N*-acetyl pyrrole [4] rearranges into *C*-acetyl pyrrole (boiling point 181°). Di-*N*-pyrryl ketone boils at 238° without decomposition, but when heated in a sealed tube at 250°, rearrangement sets in:



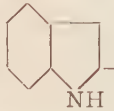
[1] Pictet, *Ber.* **37**, 2792 (1904); **38**, 1947 (1905).
[2] Pictet and Crepieux, *Ber.* **28**, 1905 (1895).
[3] Pictet, *Ber.* **37**, 2797 (1904).
[4] Ciamician and Magnaghi, *Ber.* **18**, 416, 1828 (1885).

Another pyrolysis of similar type [5] is the rearrangement at 700° of *N*-(*α*-pyridyl)-pyrrole into a mixture of *α*-pyridyl-*α*-pyrrole and *α*-pyridyl-*β*-pyrrole:



Wibaut [6] has also found that if *α*,*α*-nicotyrine is heated at 700-740° the major reaction is one of rearrangement into 2-(*α*-pyridyl)-5-methyl pyrrole. Pyridine is, however, formed also, and this may account for the small amount of *α*,*α*-dipyridyl which was found.

The change of a 5-membered to a 6-membered ring has already been mentioned in the change of methyl pyrrole into pyridine (10 percent yields):

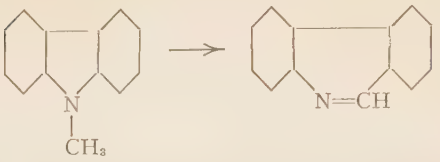
Similarly, fair yields of quinoline are formed [7] by passing 2-methyl indole, 

, through a hot tube. Since *N*-benzyl pyrrole pyrolyzes into *β*-phenyl pyridine (Pictet), it demonstrates that either a benzyl group or a methyl group may function in this manner.

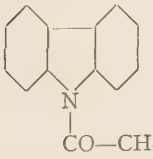
Tripyrrole, $C_{12}H_{15}N_3$, undergoes a breakdown [8] at sufficiently elevated temperature into ammonia, pyrrole and indole. Similarly, diethyl-dipyrrole, $(C_4H_3(Et)=NH)_2$, pyrolyzes [9] into ammonia and diethyl-indole, $C_8H_5(Et)_2N$.

Although carbazole is related to pyrrole, it differs in that the *α*-positions are blocked for purposes of rearrangement. Therefore, *N*-methyl carbazole cannot rearrange into a *C*-methyl carbazole, but it can simulate the indoles in forming phenanthridine, a compound with a 6-membered heterocyclic ring. This it does at high temperatures: [10]

[5] Wibaut, *Verslag. Akad. Wetenschappen Amsterdam* **35**, 552 (1927); *Chem. Abstracts* **21**, 3362 (1927).
[6] Wibaut and Dingemanse, *Rec. trav. chim.* **45**, 671 (1926).
[7] Pictet, *Ber.* **38**, 1949 (1905). Concerning the reverse process, *see* Padua and others, *Atti accad. Lincei* [5] **15**, II, 113 (1906); **17**, I, 728 (1908).
[8] Dennstedt and Voigtländer, *Ber.* **27**, 476 (1894).
[9] Dennstedt, *Ber.* **21**, 3429 (1888); *Chem. Zentr.* **1901**, II, 1135; Ciamician's address, *Ber.* **37**, 4235 (1894).
[10] Pictet, *Ber.* **38**, 1950 (1905).

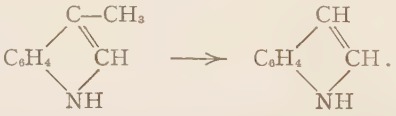


The *N*-acyl carbazoles do not pyrolyze according to either of these mechanisms, but instead they change into carbazole. With *N*-palmityl carbazole, *N*-nonoyl carbazole, and *N*-phenoxyacetyl carbazole:

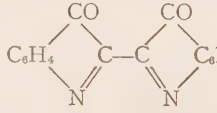


, wherein R represents $C_{14}H_{29}$, C_7H_{15} and C_6H_5O respectively, the transformation [11] into carbazole occurs at the respective melting points (91°, 73° and 121°). The fate of the residue, which contains the elements of a ketene, R—CH=CO, is undetermined. It may be pointed out that the acyl carbazoles are essentially amides, and the acyl carbazoles may, therefore, pyrolyze in the manner of amides (see Chapter 19).

Skatole [12] vapors, if passed through a red hot tube filled with porcelain, give a combustible gas and a distillate, whose aqueous solution gives a test for indole. Thus:



In fact, this transformation may be realized by heating small amounts of skatole in a small test tube over a free flame.

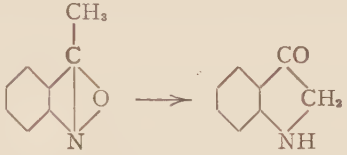
Dehydroindigo,  , sublimes to indigo, and melts with decomposition [13] at 210-215°, giving gaseous products. When it is heated in a high boiling solvent, part of the substance is reduced to indigo at the expense of another part, which is simultaneously oxidized to isatin and other products.

Dry distillation of indigo led Otto Unverdorben in 1826 to the discovery of aniline (then named "krystallin"). This was published by Trommsdorf in October 1826 in his *Neues Journal der Pharmazie*, and it has been recently referred to by O. Schlenk, *Z. angew. Chem.* **39**,

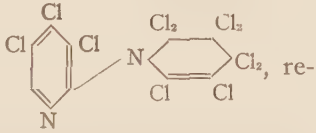
[11] Copisarow, *J. Chem. Soc.* **113**, 816 (1918).
[12] Fileti, *Gazz. chim. ital.* **13**, 378 (1883).
[13] Kalb, *Ber.* **42**, 3643 (1909).

757 (1926), and by Darmstaedter in the News Edition of *Ind. Eng. Chem.* for Oct. 10, 1927 (p. 9).

Indoxyl may be prepared [14] by heating C-methyl anthranil (α-methyl-β,γ-benzoisoxazole):

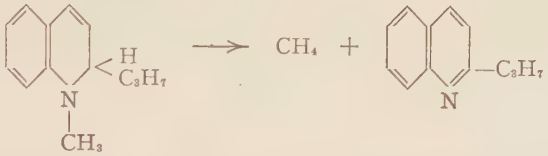


The formation of graphite-like substances by the pyrogenic decomposition of tetraiodopyrrole, tetraiodofuran, etc., has been related on page 144. The highly chlorinated compound,

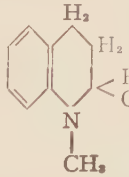


related to pyridine, undergoes pyrolysis [15] at 230-240° and 20 mm. into 2 molecules of pentachloropyridine, C_5Cl_5N.

By distilling 1-methyl-2-propyl-dihydroquinoline [16] (270°), methane is evolved to a considerable extent:



By long refluxing, a 40 percent yield of 2-propyl quinoline may be realized. Simultaneously, 10 percent of 1-methyl-2-propyl-tetrahydroquinoline,



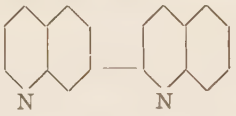
appears.

Reminiscent of the change from benzene into diphenyl, pyridine undergoes pyrolysis [17] into dipyridyl. Chiefly this is α,α-dipyridyl, but it is mixed with some of the α,β- and some of the α,γ-isomer. The α-methyl homolog,

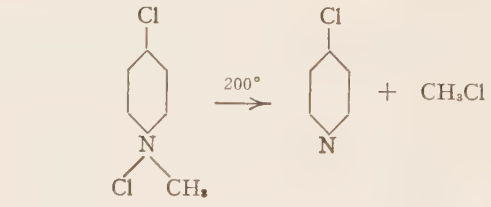
similarly yields α,α-dipicolyl; α,α-di-

[14] Bamberger and Elger, *Ber.* **36**, 1624 (1903).
[15] Sell and Dootson, *J. Chem. Soc.* **75**, 980 (1899); **79**, 899 (1901).
[16] Meisenheimer and Schütze, *Ber.* **56**, 1353 (1923).
[17] Meyer and Hofmann-Meyer, *J. prakt. Chem.* **102**, 287 (1921).

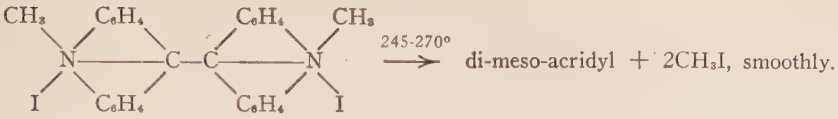
methylpyridine pyrolyzes into tetramethyl-dipyridyl, and α,α,γ-trimethyl-pyridine into a dicollidyl.

The pyrogenic decomposition of quinoline is similar. Poor yields of biquinolyl,  , result when the vapors of quinoline [18] are passed through an iron tube heated to dull redness. The sulfonic acid, , also gives a 10 percent yield of biquinolyl [19] by dry distillation.

N-Ethyl-pyridinium iodide rearranges (sealed tube) at 290° into a mixture [20] of the hydriodides of α- and γ-ethylpyridine; none of the β-isomer is formed. Ten or fifteen degrees higher, much ammonia is evolved, and there is also formed a hydrocarbon, thought to be ethyl benzene. From 800 grams of pyridine (in runs of about 3 grams each, admixed with twice the weight of ethyl iodide) Ladenburg isolated 667 grams of crude pyridine bases, yielding 105 grams of α- and 54 grams of γ-ethyl-pyridine, and also some α,γ-diethylpyridine. Frequently, with the methyl halide derivatives, there is simple elimination of the methyl halide, without subsequent attachment, as the following equations reveal.[21, 22, 23]

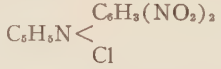


[18] Zimmermann and Müller, *Ber.* **17**, 1965 (1884).
[19] Fischer and van Loo, *Ber.* **17**, 1899 (1884).
[20] Ladenburg, *Ber.* **16**, 2059 (1883); **18**, 2961 (1885); Chichibabin, *Ber.* **36**, 2710 (1903).
[21] Fischer and Demeler, *Ber.* **32**, 1307 (1899).
[22] Michaelis and Hölken, Ann., **331**, 245 (1904).
[23] Decker and Dunant, *Ber.* **42**, 1178 (1909).



However, when 22 grams of the methiodide of 3-ethylpyridine [24] is heated at 300° in a sealed tube, there is isolated 3.6 grams of 3-ethyl-6-methyl-pyridine and only 0.5 gram of β-collidine.

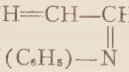
The 2,4-dinitrophenyl chloride derivative [25] of pyridine,

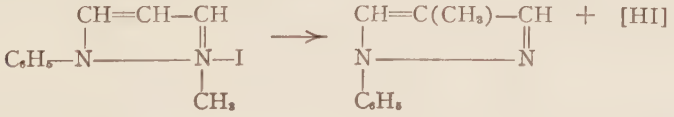


decomposes into its constituent parts by fusion (decomposition begins at 200°). The bromide behaves similarly at 225°. Pyridine forms a red-colored derivative with ethyl chlorocarbonate, $C_5H_5N(Cl)—CO_2C_2H_5$. This substance [26] pyrolyzes into pyridine, pyridine hydrochloride, ethyl chloride and carbon dioxide. The derivative from quinoline breaks down similarly.

2-Phenoxypyridine [27] is convertible into 1-phenylpyridone at red heat, thus establishing direct conversion of tautomeric forms without the limitation of indirect formation through the quaternary halides.

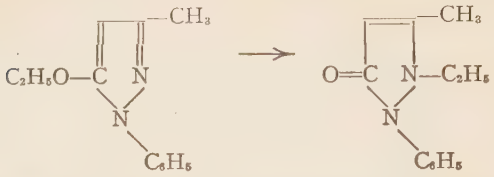
N-Heterocyclic Compounds with More Than One Nitrogen Atom Per Nucleus.

Pyrazole is stable at 300°, but related compounds show a lesser degree of stability. Thus, phenyl pyrazole,  , melts with decomposition at 178°. If the methiodide of this compound is maintained at 300°, 1-phenyl-4-methyl-pyrazole [28] is formed, among other things:

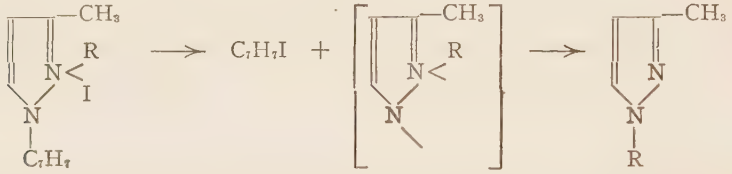


By a similar treatment (3 hours at 250°), 1-phenyl-3-methyl-5-ethoxy-pyrazole [29] rearranges into 1-phenyl-2-ethyl-3-methyl-pyrazolone-(5):

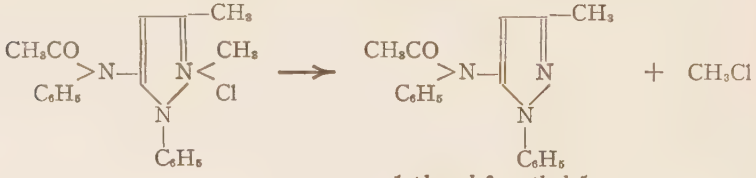
[24] Koenigs and Hoffmann *Ber.* **58**, 194 (1925).
[25] Zincke, Heuser and Möller, *Ann.* **333**, 297, 299 (1904).
[26] Hopkins, *J. Chem. Soc.* **117**, 278 (1920).
[27] Chichibabin and Jeletzky, *Ber.* **57**, 1158 (1924).
[28] Balbiano and Marchetti, *Gazz. chim. ital.* **23**, I, 486 (1893).
[29] Stolz, D.R.P. 95643; *Chem. Zentr.* **1898**, 1, 812.



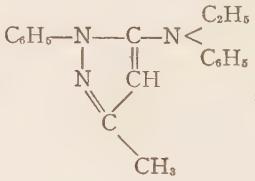
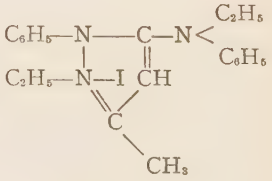
The methiodide of 1-phenyl-3-methylpyrazole [30] loses methyl iodide by dry distillation, yielding 1-phenyl-3-methyl pyrazole. Similarly, there is a simple methyl iodide elimination from 1-phenyl-5-methylpyrazole methiodide, but with the methiodide of 1-benzyl-3-methylpyrazole, benzyl iodide is eliminated and 1,3-dimethylpyrazole is formed. In like fashion, the ethiodide yields 1-ethyl-3-methylpyrazole. The 1,5-dialkyl-pyrazoles might be anticipated, but instead, the 1,3-compounds are formed:



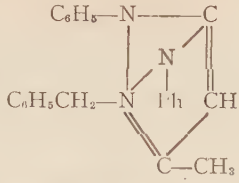
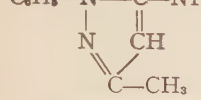
In the next illustration, again a derivative of 1-phenyl-3-methylpyrazole, methyl chloride is detached [31] by distillation:



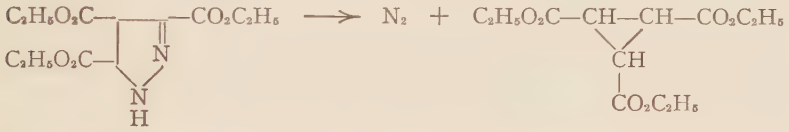
1-phenyl-3-methyl-5-acetylanilino-pyrazole

Pseudo-ethyl-anilopyrine,  , is easily prepared [32] by distilling the ethiodide of ethyl anilopyrine,  .

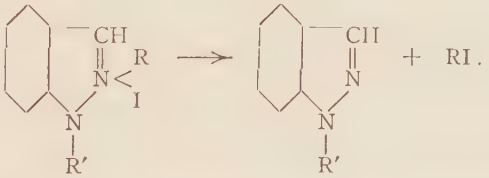
[30] von Auwers and Broche, *Ber.* **55**, 3880 (1922).
[31] Michaelis, *Ann.* **385**, 9 (1911).
[32] Michaelis and Mielecke, *Ber.* **40**, 4485, 4488 (1907).

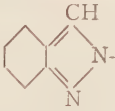
Again, if 2-benzyl anilopyrine,  , is converted into the benzyl chloride derivative and distilled, pseudobenzylanilopyrine,  , is formed.

One does not usually regard the change from a 5-membered ring to a 3-membered ring as one which may be accomplished by thermal means, but the pyrolysis [33] of 3,4,5-tricarbethoxypyrazoline into ethyl cyclopropane-tricarboxylate is one instance of this type of change:

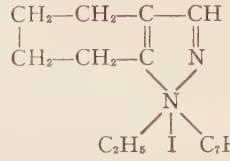
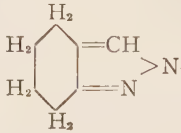


Dialkylindazolium iodides usually decompose by heat according to the following equation:

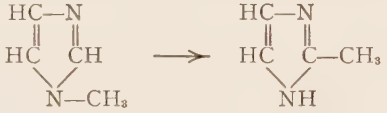


However, when R represents ethyl and R′ represents methyl, 1-methylindazole comprises [34] only three-fourths of the reaction product. The remainder is 2-ethyl-indazole,  . Neither is 1-benzyl-indazole the exclusive product formed when 1-benzyl-2-methylindazolium iodide [35] is distilled *in vacuo*. Some 2-methylindazole is formed as well. However, with 2-benzyl-1-methylindazolium iodide, 1 methylindazole is the exclusive heterocyclic reaction product. The synthesis of

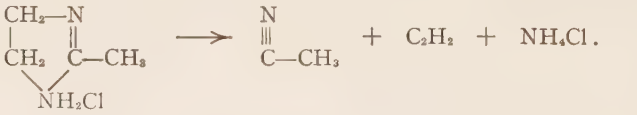
[33] Buchner, *Ann.* **273**, 229 (1893).
[34] von Auwers and Düesberg, *Ber.* **53**, 1179 (1920).
[35] von Auwers and Schaich, *Ber.* **54**, 1738 (1921).

1-ethyl-1-benzyl-tetrahydroindazolium iodide,  , may be effected by uniting ethyl iodide to 1-benzyl-tetrahydroindazole, or benzyl iodide to 1-ethyl-tetrahydroindazole. It undergoes thermal decomposition into the 2-ethyl derivative,  , and this compound is also formed [36] during the dry distillation of 2-ethyl-2-benzyl-tetrahydroindazolium iodide.

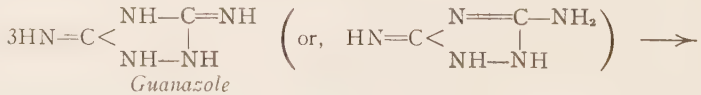
In imidazole, the nitrogens are no longer adjacent. If *N*-methylimidazole [37] is passed through a red hot tube, there is rearrangement to the *C*-methyl isomer:



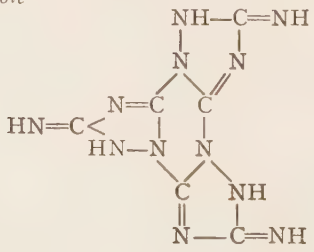
By dry distillation, lysidine hydrochloride [38] yields acetonitrile:



As the name implies, pyroguanazole is produced [39] by pyrolytic methods (30 minutes at 275°):



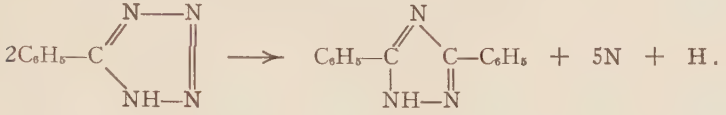
Guanazole

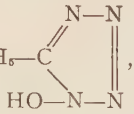


Pyroguanazole

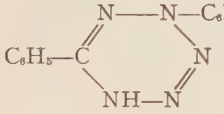
[36] von Auwers and others, *Ann.* **435**, 277 (1924).
[37] Wallach, *Ber.* **16**, 541 (1883).
[38] Ladenburg, *Ber.* **28**, 3069 (1895).
[39] Hofmann and Ehrhart, *Ber.* **45**, 2733 (1912).

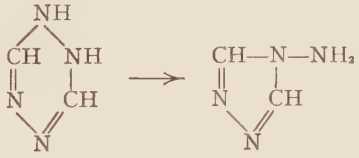
With careful heating, and with small quantities, benzenyl-tetrazotic acid [40] decomposes into diphenyl triazole. The substance explodes violently on rapid heating:



The *N*-hydroxy derivative,  , decomposes spontaneously.[41]

From 17 grams at the outset, 11 grams of a mixture of benzonitrile and water remain as a residue. The gases contain nitrogen and nitric oxide; there is no evidence for the formation of hydrazoic acid, HN_3; ammonia, NH_3; hydrazine, N_2H_4, or hydroxylamine, NH_2OH. It is interesting to record the fact that alkalies decompose this compound into sodium hyponitrite, benzonitrile and nitrogen.

When 1 - (2,4 - dibromophenyl) - 5 - phenyl - 1,4 - dihydropentazine,  , is rapidly heated [42] in a long glass tube, opened at one end, there is a puff of black smoke. Benzonitrile may be identified as a reaction product. At the melting point (126°) of 1,2,4,5-tetrazine-1,2-dihydride, there is partial decomposition [43] into ammonia and partial rearrangement into *N*-amino-1,2,4-triazole:



[40] Lossen and Statius, *Ann.* **298**, 99 (1897).
[41] Forster, *J. Chem. Soc.* **95**, 187 (1909).
[42] Chattaway and Parkes *J. Chem. Soc.* **1926**, 113.
[43] Curtius, Darapsky and Muller, *Ber.* **40**, 821, 836, 1184 footnote (1907).

CHAPTER 24.

SULFUR COMPOUNDS.

Carbon Oxysulfide.

Two reactions prevail in the pyrogenic decomposition of carbon oxysulfide [1] at temperatures between 600-1100°:

$$COS \rightleftharpoons CO + S;$$

and

$$2COS \rightleftharpoons CO_2 + CS_2.$$

The possible side reactions of:

$$CS_2 \longrightarrow C + 2S, \quad \text{or} \quad 2CO \longrightarrow C + CO_2,$$

are negligible. The second reaction (giving $CO_2 + CS_2$) is endothermic, and its velocity is slow. The equilibrium velocity of the first reaction is high in either direction. At atmospheric pressure and a temperature of 800°, 64 percent of carbon oxysulfide is dissociated into carbon monoxide and sulfur; at 950°, 76 percent results.

Thiocarbonic Acid.

Thiocarbonic acid, H_2CS_3, is a heavy red oil which pyrolyzes [2] at the boiling point, 50°; the products are hydrogen sulfide, carbon disulfide and sulfur. Since carbonic acid is far less stable, it is evident that the sulfur in thiocarbonic acid is the responsible factor. A similar relationship holds in the ethyl acid esters:

$$[C_2H_5O—CO—OH] \text{ unknown}, \longrightarrow C_2H_5OH + CO_2$$
$$[C_2H_5O—CO—SH] \text{ unknown}, \longrightarrow C_2H_5OH + COS$$

$C_2H_5O—CS—SH$, a known [3] compound, is an oil which decomposes at 24° into ethyl alcohol and carbon disulfide.

Xanthates.

The xanthates are more stable, but by distillation they produce carbon oxysulfide. With aliphatic groups, mercaptans and unsaturated compounds are formed, whereas with aromatic substances, thioethers

[1] Stock and Seelig, *Ber.* **52**, 681 (1919); Stock, Siecke and Pohland, *Ber.* **57**, 719 (1924).
[2] O'Donoghue and Kahan, *J. Chem. Soc.* **89**, 1812 (1906).
[3] Zeise, *Berz. Jahresber.* **3**, 83 (1824); **16**, 302 (1837).

result from the pyrolysis. In the aliphatic or alicyclic series, this is frequently a convenient means of producing unsaturated compounds. To illustrate: [4, 5, 6]

$$CH_3—S—CS—O—(C_{10}H_{17})\,[\text{thujyl}] \longrightarrow COS + \underset{\textit{thujene}}{C_{10}H_{16}} + CH_3SH$$

$$CH_3—S—CS—O—(C_{27}H_{45})\,[\text{cholesteryl}] \xrightarrow{200°} COS + CH_3SH + C_{27}H_{44}$$

($C_{27}H_{44}$ is a mixture of α- and β-cholestylene)

$$C_6H_5—S—CS—O—C_2H_5 \xrightarrow{\text{heat}} COS + C_6H_5—S—C_2H_5.$$

Metallic Xanthates.

Carbon disulfide and carbon oxysulfide are formed from most xanthates by distillation. This is true with potassium xanthate,[7] $C_2H_5O—CS—SK$; and also at 350° with the xanthates [8] of barium, iron, cobalt, zinc, lead and tin. The liquid products also contain ethyl alcohol, ethyl mercaptan, ethyl sulfide and ethyl disulfide; and the gases contain hydrogen sulfide and carbon dioxide. The nickel and silver xanthates yield exclusively the ethyl ester, $C_2H_5O—CS_2C_2H_5$, and this is also largely the case with the copper and mercury salts.

Sodium Thiobenzoate.

Sodium thiobenzoate, $C_6H_5CO—SNa$, changes [9] into tetraphenylthiophene ("thionessal") by dry distillation. This heterocyclic compound may also be prepared by distilling benzoyl sulfide $(C_6H_5CO)_2S$; benzoyl disulfide; or by heating a mixture of desoxybenzoin and sulfur.

Browne [10] has demonstrated that potassium azido-dithiocarbonate decomposes quantitatively at 126° according to the equation:

$$KS—CS—N_3 \longrightarrow KSCN + S + N_2.$$

This reaction occurs slowly even at room temperature. The other alkali metal salts behave similarly, the sodium salt being the most stable and the cesium salt pyrolyzing with explosive violence. Azido-carbondisulfide [11] explodes almost instantly when heated above 100°, yielding free thiocyanogen:

$$(—S—CS—N_3)_2 \longrightarrow 2N_2 + (SCN)_2.$$

[4] Tshugaev, *Ber.* **32**, 3333 (1899); **33**, 3120 (1900).
[5] Tshugaev and Gastev, *Ber.* **42**, 4631 (1909); Tshugaev and Fomin, *Compt. rend.* **150**, 1435 (1910).
[6] Leuckhardt, *Ber.* **21** ref., 915 (1888).
[7] Fleischer and Hankó, *Ber.* **10**, 1293 (1877).
[8] Hébert, *Compt. rend.* **152**, 869 (1911).
[9] Fromm and Schmoldt, *Ber.* **40**, 2861 (1907).
[10] Browne and Hoel, *J. Am. Chem. Soc.* **44**, 2315 (1922); Browne, Audrieth and Mason, *ibid.* **49**, 918 (1927).
[11] Browne and von Hazmburg, *J. Am. Chem. Soc.* **48**, 2385 (1926).

At 80°, the explosion occurs in ten to twelve seconds; at 85°, in four to six seconds; and at 100°, in one to one and one-half seconds.

The pyrolysis of thiocarbamide-glycollic acid has been mentioned on page 590; of acetyl thiosalicylic acid on page 352; and of ethyl thiocarbamate on page 582.

Mercaptans.

Very little study has been given to the pyrolysis of mercaptans. Octyl mercaptan,[12] which boils at 198-200°, is stated to yield octyl sulfide and hydrogen sulfide readily when heated. For a long time, it was considered that Kekulé's synthesis of ethyl mercaptan from alcohol and phosphorus pentasulfide could be interpreted through a simple reaction mechanism. However, it has recently been shown[13] that an intermediate compound, $S{=}P(OC_2H_5)_2SH$, is formed, and that it is this compound which yields ethyl mercaptan by pyrolysis.

Ethyl nitrosyl mercaptide[14] is fairly stable at room temperature (2 percent decomposes at 13° in 4.5 hours), but at 70-130° it undergoes complete and irreversible scission in 2 hours' time into diethyl disulfide and nitric oxide:

$$2C_2H_5{-}S{-}NO \longrightarrow (C_2H_5)_2S_2 + 2NO.$$

Isoamyl mercaptan[15] gives large quantities of hydrogen sulfide as a decomposition product at 496°. In this work, the liquid was dropped into a sloping tube at a rate of about 0.5 cc. per minute; the length of the tube in the heating zone was 68 cm., and its internal diameter, 13.5 mm. About 7 to 8 percent of free sulfur is formed, and also hydrocarbon gases and a tarry residue. No sulfide or thiophene derivatives seem to be formed. Since hydrogen sulfide and tarry residues are invariably formed in the pyrolysis of mercaptans or sulfides, Faragher and Morrell suggest that we have here the usual cracking reaction of the hydrocarbons as a secondary result of the decomposition of the organic sulfur compounds.

On the basis of the few known facts regarding the pyrolysis of mercaptans, it is difficult to construct a hypothetical mechanism for the reaction. However, mercaptans are definitely related to alcohols, and also to amines, which are alcohols in the ammonia system (p. 290). It

[12] Kahn, *Bull. soc. chim. Roum.* **5**, 70 (1923); *Chem. Abstracts* **18**, 1467.
[13] Pishchimuka, *J. Russ. Phys. Chem. Soc.* **56**, 11 (1925); *Chem. Abstracts* **19**, 2808 (1925); *J. Chim. Ukraine* **1**, 87; *Chem. Abstracts* **20**, 2816 (1926).
[14] Lecher and Siefken, *Ber.* **59**, 1314 (1926).
[15] Faragher, Morrell and Comay, *Ind. Eng. Chem.* **20**, 527 (1928).

has already been shown that the pyrolysis of ethyl alcohol and ethyl amine is surprisingly similar:

$$CH_3—CH_2OH \begin{cases} \nearrow CH_2{=}CH_2 + H_2O \\ \searrow CH_3—CHO + H_2 \end{cases}$$

and

$$CH_3—CH_2NH_2 \begin{cases} \nearrow CH_2{=}CH_2 + NH_3 \\ \searrow [CH_3—CH{=}NH] + H_2 \end{cases}$$

$$[CH_3—CH{=}NH] \longrightarrow CH_3—C{\equiv}N + 2H_2$$

One might argue from analogy, therefore, that ethyl mercaptan should also undergo a pyrolysis in two directions, as the primary effect:

$$CH_3—CH_2SH \begin{cases} \nearrow CH_2{=}CH_2 + H_2S \\ \searrow [CH_3—CH{=}S] + H_2 \end{cases}$$

The fate of the thioacetaldehyde is problematical. It is known (see p. 704) that the polymer of thiobenzaldehyde pyrolyzes into sulfur and stilbene at 190°:

$$2(C_6H_5CHS)_3 \longrightarrow 3C_6H_5CH{=}CHC_6H_5 + 6S;$$

at higher temperatures, tetraphenylthiophene is produced. It is known also that acetaldehyde merely pyrolyzes into carbon monoxide and methane. Thioacetaldehyde, therefore, might break down into butene-2 and sulfur, or into methane and a transient [CS] which presumably would disproportionate into carbon and carbon disulfide. Neither hydrogen nor carbon disulfide has been mentioned as a product of the thermal decomposition of mercaptans but further study may reveal their presence. Some of the hydrogen may, of course, be consumed in the transformation of olefines into paraffins.

Sulfides.

From 30 grams of diethyl sulfide, pyrolyzed at an average temperature of 496°, Faragher, Morrell and Comay (*loc. cit.*) obtained 19 grams of products of decomposition, exclusive of gaseous hydrocarbons. About a 10 percent yield of mercaptan was found. Hydrogen sulfide was also produced in considerable amounts.

Isoamyl Sulfide.

One hundred grams of this substance treated similarly was found to yield 85 grams of liquid decomposition products. Only a small quantity of mercaptans which were identified as *iso*amyl mercaptan, and

thiophene derivatives as determined by the indophenin reaction, were found. The remainder of the liquid was mainly undecomposed *iso*amyl sulfide. The gaseous products contained 64.1 percent of paraffin hydrocarbons, 25.9 percent of olefines, and 0.5 percent of hydrogen. Hydrogen sulfide was produced in large quantity.

Faragher and Morrell suggest two equations to account for the decomposition of alkyl sulfides. Illustrated with ethyl sulfide:

$$CH_3CH_2—S—CH_2CH_3 \longrightarrow H_2S + C_2H_4 + 2H_2 + 2C.$$
$$CH_3CH_2—S—CH_2CH_3 \longrightarrow CH_3CH_2SH + C_2H_4.$$

The simple oxygen ethers have been shown to pyrolyze almost exclusively into an aldehyde and a hydrocarbon (p. 198):

$$R—CH_2—O—CH_2—R \longrightarrow R—CH{=}O + CH_3—R.$$

Scission to an alcohol and an olefine is never apparent unless one of the groups attached to the oxygen is aromatic. In other words, ethyl alcohol and ethylene are not the products formed during the pyrolysis of ethyl ether. In this connection, therefore, it is interesting to note that the yield of mercaptan from *iso*amyl sulfide was small, and from diethyl sulfide the yield is only 10 percent. If diethyl sulfide should decompose in an analogous way to diethyl ether, then the initial products of the change would be ethane and thioacetaldehyde, or its decomposition products:

$$CH_3CH_2—S—CH_2CH_3 \longrightarrow [CH_3—CHS] + CH_3CH_3$$

Some evidence for this behavior is found in the behavior of dibenzyl sulfide towards heat.

Dibenzyl Sulfide, $C_6H_5CH_2—S—CH_2C_6H_5$.

This compound yields a variety of products[16] when it is heated. The decomposition starts at 185°, but it does not become vigorous till 262°. The products include stilbene, hydrogen sulfide, dibenzyl and toluene. In addition, tetraphenyl thiophene[17] is produced, presumably by the interaction of stilbene with sulfur or hydrogen sulfide. In fact, at 260°, hydrogen sulfide and stilbene interact to produce a 60-70 percent yield of tetraphenyl thiophene. The presence of toluene, stilbene and hydrogen sulfide is well explained on the basis of an initial equation:

$$C_6H_5CH_2—S—CH_2C_6H_5 \longrightarrow C_6H_5CH_3 + [C_6H_5—CHS]$$
$$[C_6H_5—CHS] \longrightarrow C_6H_5CH{=}CHC_6H_5 + S.$$

[16] Forst, *Ann.* 178, 371 (1875); Fromm and Achert, *Ber.* 36, 538 (1903).
[17] Baumann and Fromm, *Ber.* 24, 1456 (1891); Baumann and Klett, *Ber.* 24, 3311 (1891); Fromm and Achert, *Ber.* 36, 541 (1903).

In the presence of organic matter, sulfur should be readily reduced to hydrogen sulfide.

Diphenyl Sulfide.

The pyrolysis of diphenyl sulfide [18] gives diphenylene sulfide and benzene, as the following equations show:

$$2(C_6H_5)_2S \longrightarrow 2(C_6H_4)_2S + 4H$$
$$4H + (C_6H_5)_2S \longrightarrow H_2S + 2C_6H_6.$$

Thioxanthene, $C_6H_4\langle^{CH_2}_{S}\rangle C_6H_4$, may be obtained pyrogenically [19] from phenyl tolyl sulfide.

Other Sulfides.

Tetraphenylethylene sulfide [20] is quantitatively transformed into tetraphenylethylene and sulfur at 200°, its melting point:

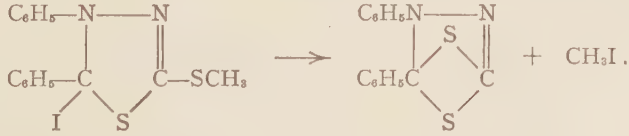
$$(C_6H_5)_2C\!-\!\!-\!C(C_6H_5)_2 \longrightarrow S + (C_6H_5)_2C{=}C(C_6H_5)_2.$$
$$\quad\ \ S$$

Tetraphenylene-ethylene sulfide, $(C_6H_4)_2C\!-\!\!-\!C(C_6H_4)_2$ (S), behaves analogously (at 220-225°), as does tetra-dimethylaminophenylethylene sulfide, $\left((CH_3)_2NC_6H_4)_2C\!-\!\!-\!C(C_6H_4N(CH_3)_2\right)_2$ (S), (in 30 min., at 210-220°).

Xanthone dibenzylmercaptol [21] changes into xanthione by heating for 15 minutes at 205°. The yield is 0.5 gram from 4 grams:

$$C_6H_4\langle^{C(SCH_2C_6H_5)_2}_{O}\rangle C_6H_4 \longrightarrow C_6H_4\langle^{CS}_{O}\rangle C_6H_4.$$

The production of endothio-thiobiazolines [22] occurs by a pyrolytic process. In the case which is cited, the change occurs at the melting point.



[18] Graebe, *Ann.* **174**, 185 (1874).
[19] Graebe and Schultess, *Ann.* **263**, 14 (1891).
[20] Staudinger and Siegwart, *Helv. Chim. Acta* **3**, 833 (1920).
[21] Schönberg and Schütz, *Ann.* **454**, 52 (1927).
[22] Busch and others, *J. prakt. Chem.* [2] **67**, 205-259 (1903).

The following transformation,[23] that of 3-keto-1,4-benzodithian-2,2′-spiro-1′,3′-benzodithiole into 2,2′-bis-1,3-benzodithiolene:

takes place above the melting point, 168°, and the reaction is rapid at 200°; yield, 0.7 gram from 3 grams. Simultaneously, there is produced some 1,3-benzodithiol-2-one, $C_6H_4<^{S}_{S}>CO$.

Disulfides.

Diacetyl disulfide[24] is not explosive, and is more stable by far than the diacyl peroxides. Ethyl thioformate tri- (or tetra-) sulfide melts with decomposition[25] at 135°, and the change may be represented as follows:

$$S_x(CS{-}OC_2H_5)_2 \longrightarrow C_2H_5{-}S{-}CS{-}OC_2H_5 + COS + (x{-}1)\ S.$$

Ethyl xanthate,[26] $C_2H_5O{-}CS_2C_2H_5$, is also formed by the distillation of a related compound, ethyl dioxysulfocarbonate, $(C_2H_5O{-}CS{-}S{-})_2$. The spontaneous decomposition of formamidine disulfide has been mentioned on page 586.

The behavior of aromatic disulfides at high temperatures may be illustrated with diphenyl disulfide, which gives rise[27] to diphenyl sulfide and diphenyl trisulfide by one hour's heating at 280° (sealed tube):

$$2C_6H_5{-}S{-}S{-}C_6H_5 \longrightarrow C_6H_5{-}S{-}C_6H_5 + C_6H_5{-}S_3{-}C_6H_5,$$

and lesser quantities of thiophenol. No free sulfur is formed in this process. α-Naphthyl disulfide behaves essentially in an analogous manner. *p,p*-Dithioacetanilide (2 hours at 240°) gives some hydrogen sulfide and acetic acid, and a mixture containing *p,p*-thioacetanilide, $(AcNHC_6H_4)_2S$. At 280° (1.5 hours), dithiosalicylic acid pyrolyzes into *o,o*-dicarboxydiphenyl sulfide, $(HO_2C{-}C_6H_4)_2S$; *o*-carboxydiphenyl sulfide, $C_6H_5{-}S{-}C_6H_4CO_2H$; and trithiosalicylic thioanhydride, $C_6H_4<^{CO{-}S{-}CO}_{S{-}{-}S{-}{-}S}>C_6H_4$. By heating methyl dithiosalicylate in a similar manner, there are formed *o,o*-dicarboxydiphenyl sulfide, a little *o*-carboxydiphenyl sulfide, and methyl thiosalicylic acid, $CH_3S{-}C_6H_4CO_2H$.

[23] Hurtley and Smiles, *J. Chem. Soc.* **1926**, 2269.
[24] Davies, *Ber.* **24**, 3549, 4251 (1891).
[25] Twiss, *J. Am. Chem. Soc.* **49**, 492 (1927).
[26] Zeise, *Berz. Jahresber.* **3**, 83 (1824); **16**, 302 (1837).
[27] Hinsberg, *Ber.* **43**, 1874 (1910).

Very recently, Faragher, Morrell and Comay [15] have investigated the behavior of several alkyl disulfides towards heat. The procedure used was the same as has been already described with *iso*amyl mercaptan, etc. In addition to the experiments at 496°, they established the fact that ethyl or *n*-propyl disulfide may be distilled with no loss, and with absolutely no formation of hydrogen sulfide. This is nearly true with *n*-butyl disulfide, but in this case there is a trace of mercaptan formed. Distillation of *isoamyl disulfide* at atmospheric pressure gives rise to hydrogen sulfide in large quantity; also there is about 9 percent of mercaptan formation. The loss is about 1 percent; the distillate is highly colored, and there is a tarry residue.

The general results are collected in the following table, for these four disulfides in their pyrogenic decomposition at 496° C.

TABLE LXI. *Pyrogenic Decomposition of Four Alkyl Disulfides.*

			Percentage and Type of Product in the Condensate from the Pyrolysis of Alkyl Disulfides at 496°, at a Rate of Flow of 0.5 cc. (Liquid) per Minute			
Name	Weight Taken Grams	Weight of Condensate Grams	S	RSH	R_2S_2	R_2S (or polymethylene sulfides or thiophanes)
Ethyl disulfide	300	117	5	8.3	68.3	11.7
n-Propyl disulfide	425	about 127	...	larger	...	...
n-Butyl disulfide	22.4	8.2	4.3	50(?)	24.7	18.8
*iso*Amyl Disulfide	413	187	3.3	33	40.4	20.2

A summary of products obtained in this manner from *ethyl disulfide* is: hydrogen sulfide, sulfur, ethyl mercaptan, alkyl sulfides (probably ethyl sulfide as shown by the reaction with mercurous nitrate), and thiophene. In addition, unsaturated and saturated gaseous products are also obtained, which, on analysis, show 67.1 percent of olefines and 11.7 percent of paraffins. There is approximately 0.1 percent of hydrogen. The residue is a pitchy material.

n-Propyl disulfide at 496° gives: hydrogen sulfide, sulfur, *n*-propyl mercaptan and an alkyl sulfide (probably *n*-propyl sulfide). Also, a derivative of thiophene, probably 3,4-dimethylthiophene, and a large quantity of a substance (about 70 percent sulfur) of definite crystalline form not yet identified are produced. The last melts at 84.5° and boils at a temperature of 180-182° and 25 mm. pressure. The gases of this decomposition, exclusive of hydrogen sulfide, are 76.6 percent olefines, and 14.6 percent paraffins. Hydrogen, apparently, is absent.

A larger quantity of propyl mercaptan is formed from propyl disulfide, than ethyl mercaptan from ethyl disulfide.

The products from the pyrolysis of *n-butyl disulfide* have not been identified with certainty. The gases analyzed: 66.1 percent paraffins, 19 percent olefines, and 0.15 percent of hydrogen.

The products from *isoamyl disulfide* were identified as: hydrogen sulfide, sulfur, *iso*amyl mercaptan, *iso*amyl sulfide, a homolog of thiophene, and gases (44.5 percent paraffins and 13 percent olefines; no hydrogen).

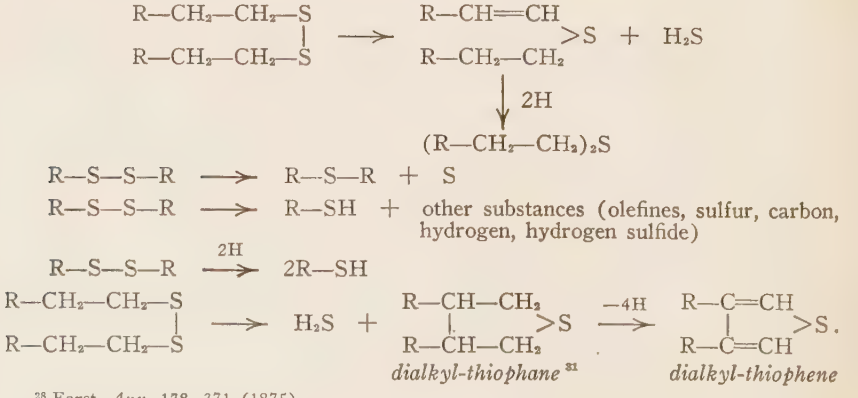
Among other substances, tetraphenylthiophene [28] is formed during the dry distillation of *dibenzyl disulfide*. The same compound is formed when the polymer of thiobenzaldehyde [29] is dry distilled. Good evidence that this reaction proceeds through stilbene and sulfur as intermediate products, is afforded by the fact that these compounds are actually formed at the lower temperature of 190°.

$$2(C_6H_5CHS)_3 \longrightarrow 3C_6H_5CH{=}CHC_6H_5 + 6S.$$

The distillation of *dibenzohydryl disulfide* gives rise to the formation of small amounts of tetraphenyl ethylene and hydrogen sulfide, but chiefly the change [30] is in accordance with the following equation:

$$((C_6H_5)_2CH)_2S_2 \longrightarrow (C_6H_5)_2CS + (C_6H_5)_2CH_2 + S.$$

Faragher, Morrell and Comay [15] have suggested a number of hypothetical reactions to explain the course of pyrolysis of the alkyl disulfides. It must be realized that these suggestions are tentative, but at least, they furnish a satisfactory picture of the rather complex decompositions.



[28] Forst, *Ann.* **178**, 371 (1875).
[29] Laurent, *Ann.* **38**, 320 (1839); **52**, 354 (1844); Baumann and Fromm, *Ber.* **24**, 1456 (1891).
[30] Wuyts, *Ber.* **36**, 864 (1903).
[31] Grischkewitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.* **48**, 901 (1916); *J. Chem. Soc Abst.* **112**, 155 (1917).

In addition to these reactions, there are always the secondary reactions of decomposition of the substances which are formed.

Petroleum which has been subjected to the sodium plumbite treatment contains some lead mercaptides in solution. At the high temperature of distillation, these are pyrolyzed [32] into volatile dialkyl sulfides:

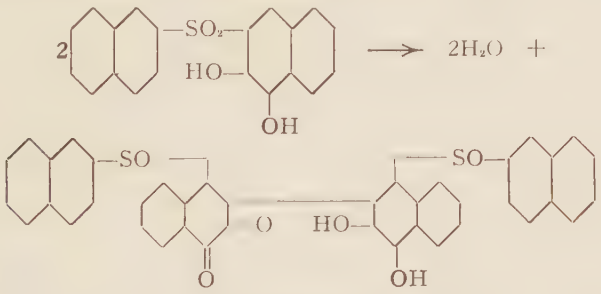
$$(RS)_2Pb \longrightarrow R_2S + PbS.$$

Thus, the petroleum distillate contains sulfur compounds, which, however, do not give the doctor test. Therefore, a "sweet" product results. Invariably, there is a black deposit of lead sulfide in the still when this method of refining is employed. Metallic sulfides, particularly of the heavy metals, are also easily formed [33] by heating the salts of thiocarboxylic acids.

When flesh products [34] in general (from a study of fish flesh) are heated above 100°, some of the *cystine* is destroyed, and the hydrogen sulfide derived therefrom may be detected in the product providing the gas is not oxidized by the material (fresh flesh) during the heating process.

Sulfones.

Sulfones have been very little studied for their behavior at high temperatures. At 200°, sulfone-diacetic acid,[35] $SO_2(CH_2CO_2H)_2$ passes into dimethyl sulfone (see p. 418). This, however, is a pyrolysis of the carboxyl group. A rather complex sulfone, 1-β-naphthalenesulfonyl-3,4-dihydroxynaphthalene [36] becomes dehydrated at 170-180°. The resultant compound is the dimer of a quinone of the *iso* series:



Tetraphenylethylene-sulfone,[37] $\begin{matrix}(C_6H_5)_2C\\ |\\ (C_6H_5)_2C\end{matrix}>SO_2$, and two other isomers

[32] Morrell, *Ind. Eng. Chem.* **18**, 735 (1926).
[33] Tarugi, *Gazz. chim. ital.* **25**, I, 341 (1895); **27**, I, 316 (1897); **27**, II, 153 (1897); Schiff and Tarugi, *Ber.* **27**, 3437 (1894).
[34] Almy, *J. Am. Chem. Soc.* **49**, 2540 (1927).
[35] Lovén, *Ber.* **17**, 2819 (1884).
[36] Hinsberg, *Ber.* **58**, 1335 (1925).
[37] Staudinger and Pfeuninger, *Ber.* **49**, 1941 (1916).

obtained from it, of which one is $C_6H_4<^{CH(C_6H_5)}_{C(C_6H_5)_2}>SO_2$, by crystallization from benzene or by heat alone, at 150-160° in a vacuum all give sulfur dioxide and a hydrocarbon, $C_{26}H_{20}$, which is an isomer of tetraphenylethylene.

There is a vigorous reaction at the melting point of benzoic acid-*o*-thionylhydrazone,[38] as sulfur dioxide is detached from the molecule:

$$C_6H_4<^{CO_2H}_{NH-N=S=O} \longrightarrow SO_2 + C_6H_4<^{CO}_{NH}>NH.$$

Out of a possible 23 percent, 15.3 percent of sulfur dioxide is liberated [38a] at 150° from benzyl disulfoxide, $(C_6H_5CH_2)_2S_2O_2$. The residue contains benzyl mono- and di-sulfides, and smells of benzaldehyde and benzyl mercaptan.

Sulfonates.

Methanesulfonic acid is a syrup which is stated [39] to undergo decomposition above 130°. Billeter, however, has shown [40] that this is in error. At 10 mm., the substance boils at 167° without decomposition. Sulfoacetic acid, $HO_3S—CH_2—CO_2H$, has already been mentioned on p. 340, as has *p*-sulfamido-benzoic acid on p. 346.

Sulfo*iso*propyl succinic acid [41] changes into terebic acid by heating *in vacuo* at a bath temperature of 160-170°. The yield, after purification, is over 30 percent:

$$(CH_3)_2C(SO_3H)—CH(CH_2CO_2H)—CO_2H \longrightarrow (CH_3)_2C(O—CO)—CH_2 + SO_2 + H_2O.$$

Bromoacetyl sulfuric acid [42] is a mixed acid anhydride. When heated, it rearranges into the isomeric bromosulfoacetic acid:

$$CH_2Br—CO—O—SO_3H \longrightarrow HO_3S—CHBr—CO_2H.$$

The reaction is exothermic, and the yield exceeds 70 percent of the theoretical. In turn, bromosulfoacetic acid disproportionates at its melting point, 119.5°:

$$2HO_3S—CHBr—CO_2H \longrightarrow HO_3S—CH_2—CO_2H + HO_3S—CBr_2—CO_2H.$$

Simultaneously, some of the dibromosulfoacetic acid becomes decarboxylated:

$$HO_3S—CBr_2—CO_2H \longrightarrow CO_2 + CHBr_2—SO_3H.$$

[38] Klileisen, *Ber.* **27**, 2555 (1894).
[38a] Smythe, *J. Chem. Soc.* **121**, 1400 (1921).
[39] Beilstein, "Handbuch der Organischen Chemie," III, 1, p. 369.
[40] Billeter, *Ber.* **38**, 2019 (1905).
[41] Koenigs and Hoerlin, *Ber.* **26**, 2047 (1893).
[42] Backer, *Rec. trav. chim.* **44**, 1056 (1925).

Benzene sulfinic acid [43] undergoes a simultaneous oxidation and reduction when it is heated at 130° in the presence of water:

$$3C_6H_5SO_2H \longrightarrow C_6H_5SO_3H + C_6H_5SO_2—S—C_6H_5.$$

Hydrocarbons, together with phenyl sulfones, are formed when aryl sulfonic acids are subjected to distillation:

$$C_6H_5SO_3H \longrightarrow C_6H_6 + [SO_3].$$

The rupture is more easily accomplished,[44] however, by distilling ammonium benzene sulfonate. Although the chief product of the reaction is *benzene,* some benzenesulfonamide appears as a sublimate. In the distillate may be found diphenyl, diphenyl sulfide, diphenyl sulfone, thiophenol and traces of quinoline. Caro's method [45] of desulfonation is a modification of this. The lead sulfonate is intimately mixed with one quarter of its weight of ammonium chloride and the mixture dry-distilled. In addition to the desulfonated substance, the crude distillate contains high amounts of mercaptans. Stenhouse [46] has investigated the behavior of the sodium, calcium and ammonium salts of benzenesulfonic acid towards dry distillation. The ammonium salt becomes dehydrated into benzenesulfonamide. At much higher temperatures, and from a copper retort, the calcium salt gives one-sixteenth of its weight of oily distillate, whereas the sodium salt gives from one-fifth to one-fourth of its weight. Of the latter, about one-quarter is thiophenol; two-thirds is diphenyl sulfide; and most of the remainder is diphenylene sulfide. In this connection, Stenhouse pointed out that the lead salt of thiophenol changes at 280° into lead sulfide and diphenyl sulfide.

Sodium ethyl-thiosulfate disproportionates with ease [47] in diethyl disulfide and sodium dithionate:

$$2C_2H_5S—SO_3Na \longrightarrow (C_2H_5)_2S_2 + Na_2S_2O_6 \text{ (which gives } Na_2SO_4 + SO_2).$$

The methyl esters of aromatic sulfonic acids are exceedingly resistant to heat, but with other esters there is a general pyrolysis into the sulfonic acid: [48]

$$Ar—SO_3—CH_2CH_2R \longrightarrow ArSO_3H + RCH=CH_2 \text{ (or a cyclic polymer)}.$$

In the case of *ethyl benzenesulfonate,* the decomposition proceeds almost quantitatively into benzenesulfonic acid and ethylene. The strongly acidic nature of the sulfonic acid frequently inhibits the isolation of the unsaturated compound as such. Thus, although the *allyl ester* is

[43] Otto, *Ann.* **145**, 317 (1867).
[44] Egli, *Ber.* **18**, 575 (1885).
[45] Mentioned by Victor Meyer, *Ber.* **16**, 1468 (1883).
[46] Stenhouse, *Ann.* **140**, 284 (1866); **149**, 247 (1869).
[47] Bunte, *Ber.* **7**, 647 (1874); Otto and Rössing, *Ber.* **25**, 989 (1892).
[48] Foldi, *Ber.* **60**, 656 (1927).

exceedingly thermolabile, the formation of a black tar is the only evidence of allene as a decomposition product. Fresh samples of this ester decomposes into benzenesulfonic acid at 186°. The reaction is very exothermic.

Benzyl benzenesulfonate decomposes at 125° into benzenesulfonic acid and a polymer of phenylmethylene, ($C_6H_5CH=$). With no hydrogens in the β-position, it is rather surprising that this ester should pyrolyze so readily when the methyl ester is so stable. The β-chloroethyl ester gives good yields of vinyl chloride in this pyrolysis, but the reaction proceeds less smoothly than with the ethyl ester:

$$C_6H_5SO_3—CH_2CH_2Cl \longrightarrow C_6H_5SO_3H + CH_2=CHCl.$$

Similarly:

$$C_6H_5SO_3—CH(CH_2Cl)_2 \longrightarrow C_6H_5SO_3H + CH_2Cl—CH=CHCl.$$

Still less satisfactory is the pyrolysis of ethylene di-benzenesulfonate, $C_6H_5SO_3—CH_2—CH_2—SO_3C_6H_5$. In addition to the sulfonic acid and ethylene, polymerized acetaldehyde is also formed.

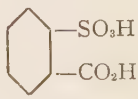
Direct distillation [49] of menthyl benzenesulfonate yields benzenesulfonic acid and a menthene. If, however, it is heated in a sealed tube at 85-90° for 6 hours, the products are benzenesulfonic acid, hexahydrocymene, dimenthene and an unidentified gelatinous substance. The menthyl naphthalene-β- and -α-sulfonates undergo an identical type of decomposition.

Other Sulfonic Derivatives.

Ethane-1,2-disulfonyl chloride [50] loses one mol of sulfur dioxide at 160°:

$$Cl—SO_2—CH_2—CH_2—SO_2Cl \longrightarrow SO_2 + Cl—CH_2—CH_2—SO_2Cl.$$

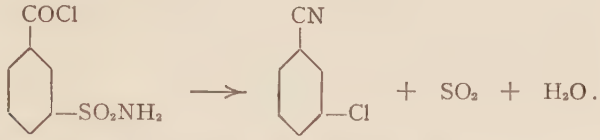
With the SO_2Cl group attached to oxygen as in $CH_3—CO—O—SO_2Cl$, there is rearrangement [51] at temperatures above 45° into $HO_3S—CH_2—COCl$. Compare the analogous rearrangement of bromoacetyl sulfuric acid (p. 706). Dichlorothionylquinol, $C_6H_4(O—SOCl)_2$, pyrolyzes [52] at 90° into *p*-benzoquinone.

If *o*-carboxy-benzenesulfonic acid,  , is heated [53] at 130° water is eliminated and the anhydride is formed, but these two sub-

[49] Patterson and McAlpine, *J. Chem. Soc.* **1927**, 349.
[50] Kohler, *Am. Chem. J.* **19**, 736 (1897).
[51] Krajcinovic, *Ber.* **59**, 2117 (1926).
[52] Green, *J. Chem. Soc.* **1927**, 503.
[53] Remsen and Dohme, *Am. Chem. J.* **11**, 334 (1889).

stances recombine on cooling unless the heating is done in the presence of a dehydrating agent, such as phosphorus pentoxide.

If *m*-carboxy-benzenesulfonamide is treated with phosphorus pentachloride to convert it to the acid chloride, distillation [54] of the resultant mixture is considered to proceed in accordance with the equation:



Since phosphorus compounds were present during the distillation, it cannot be stated whether or not this reaction is one of pyrolysis. Sulfur dioxide is also evolved [55] as *p*-chloro-benzenesulfonyl chloride, $Cl—C_6H_4—SO_2—Cl$, is distilled (in the presence of $POCl_3$) with the formation of *p*-dichlorobenzene.

At about 200°, diethyl sulfite pyrolyzes [56] into sulfur dioxide and diethyl ether (see p. 147).

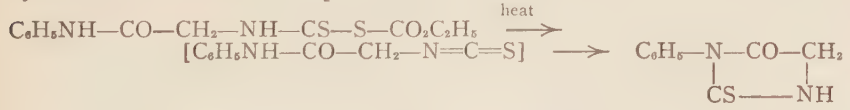
Thiocarbamates and Related Compounds.

Thiocyanogen, SCN, is isolable, but is unstable [57] at room temperature. As it breaks up, a red-brown, and finally a yellow, smoke is emitted, and the residue is a red, amorphous solid.

Between 150-200°, the thiourethanes [58] decompose into *iso*thiocyanates and mercaptans:

$$RNH—CS—SR' \longrightarrow RN{=}C{=}S + R'SH,$$

wherein R represents H, CH_3, or C_6H_5; and R′ represents CH_3, allyl, benzyl, or $RNH—CS—S—(CH_2)_x—$. An *iso*thiocyanate is presumably also the intermediate product in the next illustration, but a thiohydantoin [59] is the isolated product:



Disulfides of the general formula, $(RNH—CS—S—)_2$, namely, the N-alkyl derivatives of thiuramdisulfide,[60] pyrolyze also into *iso*-

[54] Limpricht and Uslar, *Ann.* **106**, 42 (1858).
[55] Ehrenfeld, Northwestern University, private communication.
[56] Prinz, *Ann.* **223**, 374 (1884).
[57] Söderback, *Ann.* **419**, 217 (1919).
[58] von Braun, *Ber.* **35**, 3372 (1902); **42**, 4571 (1909); Delépine, *Ann. chim.* [7] **29**, 103 (1903).
[59] Johnson, Hill and Kelsey, *Proc. Natl. Acad. Sci.* **6**, 290 (1920); *Chem. Abstracts* **14**, 3228 (1920).
[60] von Braun, *Ber.* **36**, 2259 (1903); von Braun and Stechele, *Ber.* **36**, 2275 (1903).

thiocyanates, sulfur and hydrogen sulfide unless the group R is large, in which case the products are thioureas $(RNH)_2CS$, sulfur and carbon disulfide.

If one heats the phenylhydrazonium salt of phenylhydrazine-dithio-carboxylic acid [61] (formed from $CS_2 + 2C_6H_5NHNH_2$), the type of reaction is reminiscent of urea formation from ammonium carbamate, and very probably the mechanism is the same:

$$C_6H_5NH{-}NH{-}CS{-}S{-}NH_3NHC_6H_5 \longrightarrow H_2S + CS(NHNHC_6H_5)_2.$$

Imino-thiocarbonic esters [62] produce mercaptans and thiocyanates by gentle warming:

$$(RS)_2C{=}NH \longrightarrow RSH + RSCN.$$

This reaction takes place at about 100° if R represents ethyl, and about 160-200° if R represents benzyl. If, in this reaction, R represents methyl, then trimethyl thiocyanurate, $(CH_3SCN)_3$, is formed (80-100°) instead of the thiocyanate.

The quaternary ammonium sulfides [63] of the general formula $(RN(CH_3)_3)_2S$ decompose smoothly between 200-300° into dimethyl sulfide and a tertiary amine:

$$(RNMe_3)_2S \longrightarrow 2RNMe_2 + Me_2S.$$

These quaternary sulfides are formed by the reaction of the quaternary hydroxides with hydrogen sulfide.

Triethyl sulfonium hydroxide breaks down [64] to diethyl sulfide by heating. In fact, this change occurs to a certain extent by evaporation:

$$(C_2H_5)_3SOH \longrightarrow (C_2H_5)_2S + C_2H_4 + H_2O.$$

Rogers and Dougherty [65] have recently investigated the thermal decomposition of the hexaphenylethane-alkyl sulfides (sealed tube at 150° for 8 hours). They have shown that there is not only dissociation into triphenylmethyl and the alkyl sulfide, but also into triphenylmethyl-alkyl-methane and triphenylmethyl alkyl sulfide:

$$\begin{matrix}(C_6H_5)_3C & & R \\ & >S< & \\ (C_6H_5)_3C & & R\end{matrix} \quad \begin{matrix}\nearrow \\ \\ \searrow\end{matrix} \quad \begin{matrix}2(C_6H_5)_3C + R_2S \\ \\ (C_6H_5)_3C{-}R + (C_6H_5)_3C{-}S{-}R.\end{matrix}$$

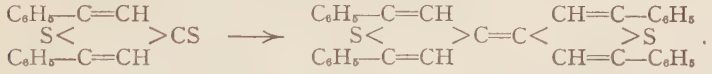
Thiophene.

The transformation of thiophene into dithienyl has been indicated on page 97. Faragher, Morrell and Comay [66] have performed experiments

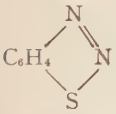
[61] Fischer, *Ann.* **190**, 118 (1877).
[62] Delépine, *Ann. chim.* [7] **29**, 138 (1903).
[63] Clarke, *J. Chem. Soc.* **103**, 1689 (1913).
[64] Alvisi, *Atti accad. Lincei* [5] **5**, II, 407 (1896); *Z. anorg. Chem.* **14**, 302 (1897).
[65] Rogers and Dougherty, *J. Am. Chem. Soc.* **50**, 152 (1928).
[66] Faragher, Morrell and Comay, private communication; *loc. cit.*

which reveal the remarkable stability of thiophene towards heat. When thiophene, admixed with purified naphtha, is passed through a tube at 496° C. or at 871° C. at the approximate rate of 0.5 cc. per minute, there is absolutely no trace of formation of hydrogen sulfide, sulfur or mercaptans. The possibility of the formation of dithienyl in these experiments was not investigated. As Faragher and Morrell point out, "the stability of thiophene suggests the reason why certain crude oils or fractions, while high in sulfur content, cause less corrosion during the cracking operation than other types of a much smaller content of sulfur. Smackover crude, containing 2.5 percent of sulfur, shows less corrosion during the cracking operation than Panhandle crude containing 0.6 percent of sulfur".

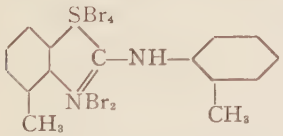
It is rather unusual to encounter compounds which melt and then, without cooling, resolidify. They are not sufficiently unusual to be classified as rarities, but nevertheless they are interesting. 2,6-Diphenylthiopyrone is such a substance. In one minute after its fusion [67] at 145° it resolidifies giving tetraphenyl-dithiopyrylene:



Another heterocyclic sulfur compound, *o*-phenylene diazosulfide,[68]



loses nitrogen at 175-200° and changes into diphenylene disulfide, $C_6H_4<\begin{matrix}S\\S\end{matrix}>C_6H_4$. 1-*o*-Toluidino-3-methylbenzothiazole hexabromide,



, loses bromine [69] at 60°.

[67] Arndt, Nachtwey and Pusch, *Ber.* **58**, 1644 (1925).
[68] Jacobson, *Ann.* **277**, 225 (1893).
[69] Hunter, *J. Chem. Soc.* **127**, 2023 (1925).

CHAPTER 25.

THE PYROLYSIS OF ORGANIC COMPOUNDS OF OTHER INORGANIC ELEMENTS.

Boron.

One of the interesting details about the element boron is that it shares but six valence electrons in its simple trivalent compounds. Thus, boron trifluoride, $F:\overset{\overset{F}{\cdot\cdot}}{\underset{\cdot\cdot}{B}}:F$, is able to accept another pair of electrons to complete its shell of eight. With alcohols, it reacts to form an addition compound,[1] presumably $F:\overset{\overset{F}{\cdot\cdot}}{\underset{\cdot\cdot F}{B}}:\overset{\cdot\cdot}{\underset{\cdot\cdot H}{O}}:R$, which decomposes at higher temperatures with the formation of $F:\overset{\overset{F}{\cdot\cdot}}{\underset{\cdot\cdot}{B}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:R$. The additive compound of boron trifluoride and dimethyl ether, $F:\overset{\overset{F}{\cdot\cdot}}{\underset{\cdot\cdot F}{B}}:\overset{\cdot\cdot}{\underset{\cdot\cdot CH_3}{O}}:CH_3$, boils without decomposition at 126-128°.

Pyroboroacetate is a reagent which is employed to determine the structure of certain classes of compounds, due to the formation of inner complexes, such as $\begin{matrix}-C-=O\\ |\quad\quad\diagdown\\ -C-O\quad\quad\diagup\end{matrix}>B(OCOCH_3)_2$. The reagent melts[2] at 150°. If it is heated at 150-160° it is quantitatively transformed into acetic anhydride and metaborate:

$$(CH_3CO{-}O)_2B{-}O{-}B(OCOCH_3)_2 \longrightarrow 2\ OB{-}OCOCH_3 + (CH_3CO)_2O.$$

Diazonium fluoborates[3] afford a very satisfactory method of synthesis of aryl fluorides; the decomposition occurs smoothly and quietly on warming the dry salt. There are no side reactions, and the yield is very high:

$$Ar{-}N_2BF_4 \longrightarrow ArF + N_2 + BF_3.$$

If Ar represents phenyl, the decomposition takes place at 121°; *p*-tolyl at 110°; and *m*-xylyl at 108°.

[1] Gasselin, *Bull. soc. chim.* [3] **7**, 17, 209 (1892); **9**, 483 (1893).
[2] Dimroth and others, *Ann.* **446**, 97 (1925).
[3] Balz and Schiemann, *Ber.* **60**, 1186 (1927).

Tellurium.

Tellurium-*O*-ethylacetylacetone trichloride, $CH_3—C(OEt)=CH—CO—CH_2—TeCl_3$, decomposes [4] with the precipitation of tellurium at its melting point, 106°, or when it is heated to 80° in solvents. Tellurium accepts two mols of methyl iodide [5] at 80°, but at 100° this compound decomposes into its constituent parts:

$$(CH_3)_2TeI_2 \longrightarrow 2CH_3I + Te.$$

Phosphorus.

Triethyl phosphine and diphenyl ketene unite to form an addition compound, which melts with decomposition [6] into its parts between 80-100°:

$$(C_2H_5)_3P\!\!<\!\!\begin{matrix}C\!=\!C(C_6H_5)_2\\ |\quad\ \ \\ O\end{matrix} \longrightarrow (C_2H_5)_3P + (C_6H_5)_2C=C=O.$$

By pyrolysis, tetramethyl phosphonium hydroxide [7] becomes transformed into trimethylphosphine oxide:

$$(CH_3)_4POH \longrightarrow CH_4 + (CH_3)_3PO.$$

Tetraethyl-phosphonium hydroxide [8] evolves ethane by heating; the reaction is obviously similar. The acetate of this base, $Et_4P—O—COCH_3$, pyrolyzes by dry distillation into triethyl phosphine, triethyl phosphine oxide, carbon dioxide, methane, ethylene and methylethyl ketone. Other salts of this type behave similarly. Briefly, the results are:

Oxalate: $(Et_4P)_2C_2O_4$, gives Et_3PO, and a little Et_3P, Et_2CO, CO, CO_2.
Benzoate: gives Et_3PO, Et_3P, C_6H_6, $C_6H_5CO_2Et$, $C_6H_5—CO—Et$, CO_2, C_2H_4.
Sulfate: $(Et_4P)_2SO_4$, gives Et_3PO and Et_3PS.
Carbonate: gives Et_3PO, CO_2, Et_3P and diethyl ketone.
Chloride: Et_4PCl, gives $Et_3PHCl + C_2H_4$, smoothly.

Methyl-triphenyl-phosphonium hydroxide [9] is very unstable. It breaks down into benzene and methyl-diphenyl-phosphine oxide:

$$[(C_6H_5)_3P(CH_3)OH] \longrightarrow C_6H_6 + (C_6H_5)_2P\!\!<\!\!\begin{matrix}O\\ \|\\ CH_3\end{matrix}.$$

[4] Morgan and Drew, *J. Chem. Soc.* **119**, 610 (1921).
[5] Vernon, *ibid.* 117, 86 (1920).
[6] Staudinger and Meyer, *Helv. Chim. Acta* **2**, 612 (1919).
[7] Cahours and Hofmann, *Ann.* **104**, *32* (1857).
[8] Letts and Collie, *Phil. Mag.* [5] **22**, 184 (1886); *J.* **1886**, 1609.
[9] Michaelis and von Soden, *Ann.* **229**, 316 (1885).

In contrast to this, benzyl-triphenyl-phosphonium hydroxide liberates toluene:

$$(C_6H_5)_3P<\begin{matrix}OH\\CH_2C_6H_5\end{matrix} \longrightarrow (C_6H_5)_3PO + C_6H_5CH_3.$$

It is obvious, therefore, that this type of pyrolysis provides a means for studying the relative firmness of attachment of radicals. Meisenheimer [10] has shown that the ease of elimination of RH from R_4POH varies according to the following sequence: allyl < benzyl < phenyl < methyl < ethyl < propyl < β-phenylethyl. Thus, allyl is least firmly held, and β-phenylethyl least easily detached. With the substituents which are least firmly held by the phosphorus atom, the decomposition occurs even in the cold, and quite rapidly by heating in water. These results are quite in contrast to the pyrolytic behavior of the quaternary ammonium hydroxides, R_4NOH, which invariably decompose into tertiary amines, and never yield amine oxides.

As is well known, phosphorus pentachloride decomposes into phosphorus trichloride and chlorine when it is heated. It is of interest to record that alkyl phosphorus tetrachloride, $RPCl_4$, dissociates [11] into phosphorus trichloride and alkyl chloride at about 135°. The alternative dissociation into $RPCl_2$ and chlorine does not occur. Phosphenyl chloride is transformed [12] into diphenyl chlorophosphine by heating at 280° in a sealed tube:

$$2C_6H_5PCl_2 \longrightarrow (C_6H_5)_2PCl + PCl_3.$$

Another case which may be considered here is the bromide of *iso*butyl phosphorous acid,[13] $(CH_3)_2CH—CH_2—O—PBr_2$, which, on distillation *in vacuo* (85° and 20 mm.), undergoes some decomposition into *iso*butyl bromide and phosphorous acid; also, there is formed a solid substance, insoluble in water, that undergoes spontaneous combustion at 40-50°. The bromide, (*iso* $C_4H_9—O)_2PBr$, behaves similarly on vacuum distillation.

The quaternary phosphonium chlorides pyrolyze into tertiary phosphines and alkyl halides (or hydrogen chloride and olefines). Tetramethylphosphonium chloride [14] is quantitatively decomposed in this manner at 300°:

$$2(CH_3)_4PCl \longrightarrow 2(CH_3)_3P + 2HCl + C_2H_4.$$

[10] Meisenheimer and others, *Ann.* **449**, 213 (1926).
[11] Guichard, *Ber.* **32**, 1576 (1899).
[12] Broglie, *Ber.* **10**, 628 (1877).
[13] Milobendzki and Krakoviecki, *Bull. soc. chim.* **41**, 932 (1927).
[14] Collie, *J. Chem. Soc.* **53**, 636 (1888); Renshaw and Bell, *J. Am. Chem. Soc.* **43**, 917 (1921).

Whereas the phenyl group is fairly readily detached from the phosphorus atom in the pyrolysis of the phosphonium hydroxides, it is the group which is least easily severed in the case of the quaternary chlorides. The position of the ethyl group also varies in the two series. The sequence [10] for the chlorides is: ethyl < benzyl < methyl < propyl < *iso*amyl < phenyl. The difference in the order of this series as compared with that from the pyrolysis of the quaternary hydroxides may be caused by the difference in the mode of pyrolysis of the two series. One forms a trivalent, and the other a pentavalent compound of phosphorus; one forms an unsaturated, and the other a saturated hydrocarbon. It is interesting to compare these data with those in Chapter 2, on electron attraction. To be comparable to the data given there, the two sequences should be listed in reverse order. Thus, for quaternary phosphonium hydroxides:

β-phenylethyl > propyl > ethyl > methyl > phenyl > benzyl > allyl;

for quaternary phosphonium chlorides:

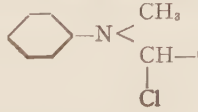
phenyl > *iso*amyl > propyl > methyl > benzyl > ethyl.

Tetraethyl-phosphonium iodide, $(C_2H_5)_4PI$, undergoes pyrolysis [6] at 150° into triethyl phosphine and ethyl iodide. The cyanogen bromide derivative of triphenyl phosphine, $(C_6H_5)_3P{<}^{CN}_{Br}$, will be referred to on a later page (p. 722).

*Iso*amyl-phosphinic acid [15] is a syrupy liquid which becomes decomposed into *iso*amyl phosphine and *iso*amyl-phosphonic acid when heated:

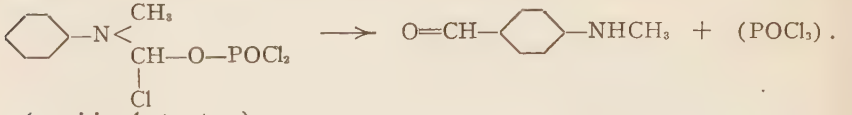
$$3C_5H_{11}{-}PO_2H_2 \longrightarrow C_5H_{11}PH_2 + 2C_5H_{11}{-}PO_3H_2.$$

Phenyl-phosphinic acid [16] behaves analogously, changing into phenyl phosphine and phenyl-phosphonic acid. The dialkyl phosphinic acids, $\begin{matrix} R_2P{=}O \\ | \\ OH \end{matrix}$, can be distilled without change.

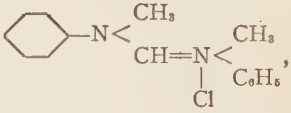
Phosphorus oxychloride reacts with *N*-methyl formanilide to produce a compound,  , which changes [17] into

[15] Guichard, *Ber.* **32** 1574 (1899)
[16] Michaelis, *Ann.* **181**, 303 (1876).
[17] Vilsmeier and Haack, *Ber.* **60**, 119 (1927).

p-methylamino-benzaldehyde at 70° (the method of p. 585 is preferable):



(provisional structure)

At the same time, another compound,  , is also formed.

For *phosphazines*, see page 646.

Bismuth.

Bismuth triethyl, $Bi(C_2H_5)_3$, explodes [18] at 150°, but it may be distilled under diminished pressure (107° at 79 mm.). The higher homologs decompose partially even by distillation in a vacuum. For example, bismuth tri*iso*amyl decomposes somewhat by distilling at 70 mm. and 190-200°. Hydrocarbons are to be found in the distillate.

Arsenic.

Arsines.

All of the primary and secondary arsines except benzyl arsine undergo pyrolysis with the liberation of arsenic. Triethyl arsine and tri-*n*-propyl arsine,[19] however, give the following equations:[20]

$$4(C_2H_5)_3As \xrightarrow[3\text{ hours}]{265^\circ} (C_2H_5As)_4 + 4C_4H_{10}$$

$$4(C_3H_7)_3As \xrightarrow[2\text{ hours}]{295^\circ} (C_3H_7As)_4 + 4C_6H_{14}$$

Benzyl arsine forms hydrogen by heating *in vacuo* at 250°:

$$4C_6H_5CH_2{-}AsH_2 \longrightarrow (C_6H_5CH_2As)_4 + 4H_2.$$

In three hours at 310°, methyl arsine is pyrolyzed (Dehn, *loc. cit.*) to methane, hydrogen and arsenic. Oxygen is excluded by an atmosphere of carbon dioxide:

$$2CH_3AsH_2 \longrightarrow 2CH_4 + H_2 + 2As.$$

Similarly, ethyl arsine changes into ethane in 3 hours at 235°, but there is a concurrent reaction into triethyl arsine:

$$3C_2H_5AsH_2 \longrightarrow (C_2H_5)_3As + 2As + H_2.$$

[18] Marquardt, *Ber.* **20**, 1518 (1887); *Ber.* **21**, 2041 (1888).
[19] Dehn, *Am. Chem. J.* **40**, 88 (1908).
[20] In view of the recent work of Palmer and Scott, *J. Am. Chem. Soc.* **50**, 536 (1928), which confirms the formula of arsenomethane as $(CH_3As)_5$, it is possible that the formula, $(C_2H_5As)_4$, and other related ones, may be in error and should be $(C_2H_5As)_5$.

Phenyl arsine appears to pyrolyze according to the latter mechanism. It changes at 310° in an atmosphere of carbon dioxide (sealed tube reaction) into triphenyl arsine, arsenic and hydrogen.

Diphenyl arsine also decomposes thermally into triphenyl arsine (3 hours at 295°):

$$6(C_6H_5)_2AsH \longrightarrow 4(C_6H_5)_3As + 2As + 3H_2.$$

In part, the triphenyl arsine is transformed into arsenic and diphenyl:

$$4(C_6H_5)_3As \longrightarrow As_4 + 6C_{12}H_{10}.$$

Di-*iso*amyl arsine, $(C_5H_{11})_2AsH$, similarly yields triamyl arsine, arsenic and hydrogen (3 hours at 240-260°), and it also yields hydrocarbons, namely, a decane, a pentane and a pentene by further pyrolysis. Dimethyl arsine undergoes a transformation [21] into a polymer of arsenomethane, $(CH_3As)_x$, by heating in a sealed tube at 335°.

At 300°, tetraphenyl diarsine [22] is converted into triphenylarsine and arsenic:

$$3(C_6H_5)_4As_2 \longrightarrow 4(C_6H_5)_3As + 2As.$$

There is no evidence of dissociation into the free radical, $(C_6H_5)_2As$. Cacodyl, Me_4As_2, changes at 340° into trimethyl arsine as one product, and the substance $(CH_3As)_5$ as the other.[23]

A polymer of arsenomethane,[24] if distilled in a current of hydrogen, pyrolyzes into trimethyl arsine and arsenic:

$$3(CH_3As)_x \longrightarrow 2As + As(CH_3)_3.$$

Arsenobenzene, $C_6H_5As{=}AsC_6H_5$, undergoes exactly the same type of pyrolysis above [25] the melting point, 208°. Arseno compounds are interesting because of the fact that unsymmetrical arseno bodies, R—As=As—R′, may be synthesized by heating [26] a mixture of two symmetrical arseno compounds.

Quaternary Arsonium Compounds.

Tetra-*n*-propyl-arsonium hydroxide, $(C_3H_7)_4AsOH$, is reported [27] to yield tri-*n*-propyl arsine oxide, or dipropyl arsinic acid, $(C_3H_7)_2AsO(OH)$, by distillation, the latter by distillation *in vacuo*.

[21] Dehn and Wilcox, *Am. Chem. J.* **35**, 9 (1906).
[22] Porter and Borgstrom, *J. Am. Chem. Soc.* **41**, 2048 (1919).
[23] Dehn, *loc. cit.*, gives $(CH_3As)_4$; *see*, however, Palmer and Scott, *J. Am. Chem. Soc.* **50**, 536 (1928).
[24] Auger, *Compt. rend.* **138**, 1707 (1904).
[25] Michaelis and Schulte, *Ber.* **14**, 912 (1881); **15**, 1953 (1882). Raiziss and Gavron, "Organic Arsenical Compounds," New York, Chemical Catalog Co. **1923**, p. 149, 150.
[26] Raiziss and Gavron, *ibid.* p. 25.
[27] Partheil and Amort, *Arch. Pharm.* **237**, 133, 137 (1899).

If the distillation [28] is performed in a current of hydrogen, dipropyl arsine is the resultant product.

Methyl-triphenyl-arsonium hydroxide melts at 125°, but if it is maintained at 100° it gradually dissociates into methanol and triphenyl-arsine. In like fashion, the following methyl-triaryl-arsonium hydroxide [29] gradually yields the triaryl-arsine about 20° below its melting point, 151°:

$$((CH_3)_3C_6H_2)_2As<\begin{matrix}C_6H_5\\ |\\ OH\\ CH_3\end{matrix} \longrightarrow CH_3OH + ((CH_3)_3C_6H_2)_2As{-}C_6H_5.$$

The following two equations [30] are examples of dehydrations which are dependent on the presence of reactive groups in the molecule.

$$(C_6H_5)_3As<\begin{matrix}CH_2{-}CO_2H\\ OH\end{matrix} \xrightarrow{100°} H_2O + (C_6H_5)_3As<\begin{matrix}CH_2\\ O\end{matrix}>CO$$

triphenyl carboxymethyl arsonium hydroxide — *triphenylarsenibetaine*

$$2(C_6H_5)_3As<\begin{matrix}CH_2\\ O\end{matrix}>C<\begin{matrix}OH\\ CH_3\end{matrix} \xrightarrow[123°]{\text{above melting point,}} H_2O + \left((C_6H_5)_3As<\begin{matrix}CH_2\\ O\end{matrix}>C{-}\begin{matrix}\\ |\\ CH_3\end{matrix}\right)_2 O.$$

Arsine Oxides.

Trisubstituted arsine oxides are readily formed by the dehydration of arsine dihydroxides, either by standing in a vacuum at 50°, or by warming to about 110° at ordinary pressures.[31] For example: at 105-110°,

$$(C_6H_5)_3As(OH)_2 \longrightarrow (C_6H_5)_3AsO + H_2O.$$

Other examples are the *dihydroxides* of phenyl-dixylyl arsine,[32] tri-α-naphthyl arsine,[33] and 10-methyl-phenoxarsine,[34] $C_6H_4<\begin{matrix}CH_3\\ |\\ As(OH)_2\\ O\end{matrix}>C_6H_4$.

Above its melting point, 120°, there is a transformation [35] of phenyl arsine oxide into triphenyl arsine and arsenic oxide:

$$3C_6H_5AsO \xrightarrow{180°} As_2O_3 + (C_6H_5)_3As.$$

[28] Partheil and Amort, *ibid.* p. 134; *Ber.* **31**, 596 (1898).
[29] Michaelis, *Ann.* **321**, 168, 232 (1902).
[30] Michaelis, *Ann.* **320**, 174 (1901).
[31] LaCoste and Michaelis, *Ann.* **201**, 244 (1880); Michaelis, *Ann.* **321**, 164 (1902).
[32] Michaelis, *Ann.* **321**, 231 (1902).
[33] *Ibid.* p. 245; Zuckerkandl and Sinai, *Ber.* **54**, 2488 (1921).
[34] Aeschlimann, *J. Chem. Soc.* **1927**, 414.
[35] LaCoste and Michaelis, *Ber.* **11**, 1887 (1878); *Ann.* **201**, 237 (1880).

This change occurs in the case of *p*-aminophenyl arsine oxide by boiling [36] a solution of its hydrochloride, $OAs—C_6H_4NH_3Cl$. A similar conversion [37] of di-*p*-tolylarsine oxide, $((CH_3C_6H_4)_2As)_2O$, into tri-*p*-tolyl-arsine may be effected by heating.

Arsenic Sulfides.

In the thermal decomposition of alkyl or aryl arsenic sulfides, RAsS, or disulfides, $RAsS_2$, arsenic trisulfide is an invariable reaction product. This is true with methyl arsine sulfide [38] and with phenyl arsine sulfide: [39]

$$3C_6H_5AsS \xrightarrow[\text{in } CO_2]{\text{at melting point, } 152^\circ} (C_6H_5)_3As + As_2S_3.$$

The literature lists two reactions for the pyrolysis of methyl arsine disulfide. According to Meyer,[40] the products are methyl sulfide and arsenic trisulfide:

$$2CH_3AsS_2 \longrightarrow (CH_3)_2S + As_2S_3,$$

whereas Dehn [41] claims that the disulfide pyrolyzes into trimethylarsine sulfide and arsenic pentasulfide:

$$3CH_3AsS_2 \longrightarrow (CH_3)_3AsS + As_2S_5.$$

At 180-195°, ethyl arsine disulfide [42] also yields triethyl arsine sulfide. Benzyl arsine disulfide, $C_6H_5CH_2AsS_2$, pyrolyzes [43] into hydrogen sulfide, arsenious sulfide and stilbene.

Arsenic Halides.

When β-chlorovinyl-dichloro-arsine, commonly known as "Lewisite", is distilled [44] at atmospheric pressure, it undergoes a disproportionation:

$$2CHCl{=}CH—AsCl_2 \longrightarrow AsCl_3 + (CHCl{=}CH)_2AsCl,$$

and in turn, when a pure sample of di-(β-chlorovinyl)-chloroarsine is distilled, it also undergoes a partial disproportionation:

$$2(CHCl{=}CH)_2AsCl \longrightarrow CHCl{=}CHAsCl + (CHCl{=}CH)_3As.$$

Lewisite may also be formed by boiling tri-β-chlorovinyl arsine with arsenic trichloride.

[36] Ehrlich and Bertheim, *Ber.* **43**, 923 (1910).
[37] LaCoste, *Ann.* **208**, 18 (1881).
[38] von Baeyer, *Ann.* **107**, 279 (1858).
[39] Michaelis and Schulte, *Ber.* **15**, 1953 (1882); Schulte, *ibid.* p. 1956.
[40] Meyer, *Ber.* **16**, 440 (1883).
[41] Dehn, *Am. Chem. J.* **33**, 135 (1905).
[42] Dehn, *Am. Chem. J.* **40**, 116 (1908).
[43] Dehn and McGrath, *J. Am. Chem. Soc.* **28**, 355 (1906).
[44] Lewis and Perkins, *Ind. Eng. Chem.* **15**, 293 (1923).

The hydrochloride of *p*-aminophenyl-dichloroarsine [45] melts with decomposition at 140°. Arsenic is severed from the nucleus, according to the following equation:

$$Cl_2As—C_6H_4—NH_3Cl \longrightarrow AsCl_3 + C_6H_5NH_2.$$

The chlorine in this compound may be replaced by bromine or iodine for the same type of pyrolysis.

Methyl dichloroarsine absorbs chlorine in the cold to produce transient crystals of methylarsine tetrachloride, and these decompose [46] into methyl chloride at about 0°:

$$CH_3AsCl_4 \longrightarrow AsCl_3 + CH_3Cl.$$

The elimination of methyl chloride by heat is general for all the compounds of the general formula $As(CH_3)_xCl_{(5-x)}$, and in fact for most pentavalent arsenic compounds which contain halogens. The decomposition occurs most readily when x is small. Cacodyl trichloride does not break down [47] till 40-50°:

$$(CH_3)_2AsCl_3 \longrightarrow CH_3Cl + CH_3AsCl_2.$$

Distillation [48] of trimethylarsine diiodide or dichloride causes a similar type of decomposition:

$$(CH_3)_3AsI_2 \longrightarrow CH_3I + (CH_3)_2AsI.$$

The yield in the case of the dichloride is 87 percent.

The aromatic analogs pyrolyze in a similar manner. Phenylarsine-tetrachloride must be heated [49] in a sealed tube at 150°:

$$C_6H_5AsCl_4 \longrightarrow C_6H_5Cl + AsCl_3.$$

Otherwise (in an open tube), there is dissociation into phenyl dichloroarsine and chlorine. The related phenylarsine oxychloride, $C_6H_5AsOCl_2$, pyrolyzes in a similar manner [50] into chlorobenzene and arsenic oxychloride. This occurs in the course of a few hours at 120°. The *p*-methyl homolog, $CH_3C_6H_4—AsOCl_2$, changes into *p*-chlorotoluene [51] by heating it at 200° in a sealed tube.

Triphenylarsine dichloride [52] decomposes by vacuum distillation:

$$(C_6H_5)_3AsCl_2 \xrightarrow{280°} (C_6H_5)_2AsCl + C_6H_5Cl.$$

diphenylchloroarsine

[45] Ehrlich and Bertheim, *Ber.* **43**, 920 (1910); Bertheim, *Ber.* **44**, 1070 (1911).
[46] von Baeyer, *Ann.* **107**, 274 (1858).
[47] von Baeyer, *ibid.* p. 263.
[48] Cahours, *Ann.* **112**, 228 (1862); Valeur and Gailliot, *Bull. soc. chim.* **41**, 1318 (1927).
[49] Michaelis, *Ber.* **10**, 622 (1877); LaCoste and Michaelis, *Ann.* **201**, 198 (1880).
[50] Michaelis, *ibid.* p. 624.
[51] LaCoste and Michaelis, *ibid.* p. 253.
[52] LaCoste and Michaelis, *Ann.* **201**, 242 (1880); *Ber.* **11**, 1888 (1878). Michaelis, *Ann.* **321**, 162 (1902).

A little variation is provided [53] in the case of cyclopentamethylene-phenylarsine-dichloride, $(CH_2)_5{-}AsCl_2$ (with C_6H_5 on the arsenic), which yields 1,5-dichloropentane by distillation *in vacuo* (150-205° and 20 mm.). The tolyl analog behaves similarly. With a hydroxyl and halogen both present on a pentavalent arsenic atom, the mode of pyrolysis is also altered. Thus, vacuum distillation (178° and 13 mm.) of $C_6H_5(CH_3)_2As{<}^{OH}_{Br}$ in a current of nitrogen gives only small amounts of either methyl bromide or methanol, but yields [54] chiefly

$$C_6H_5(CH_3)_3AsBr, \quad C_6H_5(CH_3)As(=O)(OH), \text{ and } C_6H_5(CH_3)AsBr.$$

There are also small amounts of phenyl dimethyl arsine and phenyl dibromoarsine.

The halogen in *quaternary arsonium halides* may also be detached from the molecule as an alkyl halide by thermal means. Thus, phenyl-triethyl-arsonium iodide, if heated [55] in an atmosphere of carbon dioxide, changes into phenyl diethyl arsine; and diphenyl-methyl-ethyl-arsonium iodide [56] into methyl diphenyl arsine. Since ethyl iodide is the alkyl halide which is formed in both cases, this demonstrates that it is not always the smaller group which is eliminated. The general type of pyrolysis is thus seen to be the same as with the aliphatic quaternary ammonium compounds (p. 317), but with the ammonium compounds the methyl group is detached more readily than the ethyl.

Phenyl-trimethyl-arsonium iodide [57] is decomposed into phenyl-dimethyl-arsine and methyl iodide at 248°, although in a sealed tube the compound is stable to 400°. There is apparently no tendency for the rearrangement of the methyls to the aromatic nucleus, which is so characteristic with the ammonium derivatives.

With ethyl-tri*iso*propyl-arsonium iodide,[58] two concurrent reactions are induced by heating:

$$(C_3H_7)_3As(C_2H_5){-}I \longrightarrow (C_3H_7)_3As + C_2H_5I$$

and

$$2(C_3H_7)_3As(C_2H_5){-}I \longrightarrow (C_3H_7)_3As + C_4H_{10} + (C_3H_7)_3AsI_2.$$

The latter is a rather startling departure from the general reaction.

[53] Grüttner and Wiernik, *Ber.* **48**, 1481 (1915).
[54] Steinkopf and Schwen, *Ber.* **54**, 2794, 2807 (1921).
[55] LaCoste and Michaelis, *Ann.* **201**, 213 (1880).
[56] Michaelis and Link, *Ann.* **207**, 195 (1881).
[57] Winmill, *J. Chem. Soc.* **101**, 718 (1912).
[58] Dehn, *Am. Chem. J.* **40**, 112 (1908).

Diethyl cyano arsine [59] may be synthesized by the pyrolysis of a pentavalent arsenic cyano-bromide:

$$(C_2H_5)_3As<\begin{matrix}CN\\Br\end{matrix} \longrightarrow (C_2H_5)_2AsCN + C_2H_5Br.$$

The reaction is brought about by vacuum distillation. The cyanogen bromide derivative of methyl diphenyl arsine, $(C_6H_5)_2As(CH_3)(CN)Br$, similarly loses its molecule of methyl bromide at 100°. With the corresponding derivative [60] of triphenylarsine, $(C_6H_5)_3As<\begin{matrix}CN\\Br\end{matrix}$, in order to have the same type of decomposition, phenyl bromide should be detached, but this is not the case. Instead, at 175°, a small quantity of cyanogen bromide, triphenyl arsine, cyanogen, and a brown residue are formed. This observation is quite in keeping with the result when the phosphorus analog is pyrolyzed:

$$2(C_6H_5)_3P<\begin{matrix}CN\\Br\end{matrix} \longrightarrow (C_6H_5)_3P + (CN)_2 + (C_6H_5)_3PBr_2.$$

The following equations represent similar cases of rather unusual types of arsenic halides.

$$(CH_3)_4AsI_3 \xrightarrow{\text{heat}}{}^{61} (CH_3)_2AsI + 2CH_3I.$$

$$C_6H_5(CH_3)_2AsBr_4 \xrightarrow{160^\circ} C_6H_5AsBr_2 + 2CH_3Br$$

phenyl dimethyl arsine-tetrabromide [62]

If triphenylenediarsine tetrabromide [63] is heated at 15 mm., *o*-dibromobenzene and arsanthrene bromide appear.

Arsenic Acids.

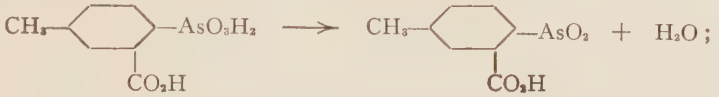
Above 140°, phenyl arsonic acid [64] gradually loses a mol of water giving the anhydride:

$$C_6H_5AsO(OH)_2 \longrightarrow H_2O + C_6H_5AsO_2.$$

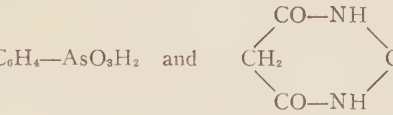
To expedite this process, it may be performed in a vacuum, or at somewhat higher temperature (usually not above 200°), or by heating in a

[59] Steinkopf and Müller, *Ber.* **54**, 846 (1921).
[60] Steinkopf and Schwen, *Ber.* **54**, 2798 (1921).
[61] Cahours, *Ann.* **122**, 215 (1962); Steinkopf and Schwen, *Ber.* **54**, 1445 (1921).
[62] Winmill, *J. Chem. Soc.* **101**, 723 (1912).
[63] McClelland and Whitworth, *J. Chem. Soc.* **1927**, 2753.
[64] LaCoste and Michaelis, *Ann.* **201**, 203 (1880).

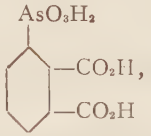
desiccated atmosphere; i.e., over phosphorus pentoxide. The following aryl arsonic acids undergo this type of pyrolysis: *o*-CH_3—C_6H_4—AsO_3H_2, by long fusion [65] at 160°; *m*-O_2N—C_6H_4—AsO_3H_2, at 180-200°; [66] *p*-benzarsonic acid, HO_2C—C_6H_4—AsO_3H_2, at 220°; [67] *m*-benzarsonic acid, at 220°; [68] *p*-methyl-*o*-benzarsonic acid,[69]



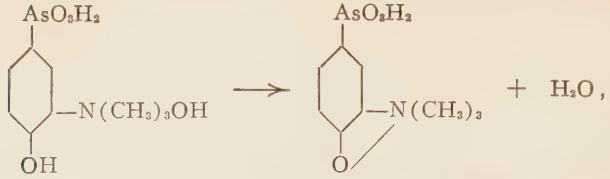
and *p*-arsanilic acid,[70] H_2N—C_6H_4—AsO_3H_2, at 100-140° and a pressure of 10 mm. over P_2O_5. The following compounds are also dehydrated by this means:



or malonylamino-arsanilic acid. With amino-arsanilic acid (3,4-diaminophenyl-arsonic acid), there is a slightly different type of dehydration, and the compound formed gives analytical values which indicate that 3 molecules of water have been expelled from two of the acid.

The anhydride of 2,3-dicarboxyphenylarsonic acid,  , may be formed by heating [71] the acid for one week at 200°. Whether or not this anhydride is of the Ar—AsO_2 type, or of the phthalic anhydride type, has not as yet been ascertained; both are reasonable possibilities. However, the anhydride obtained condenses [72] with phenol, thereby leading one to infer that it is the latter type. With the 4-isomer, it has been definitely determined [73] that two molecules of water may be driven off, giving the substance . This anhydride also condenses with phenol or resorcinol, forming compounds similar to phenolphthalein and fluorescein. The reaction:

[65] Michaelis and LaCoste, *Ann.* **201**, 255 (1880).
[66] Schmidt, *Ann.* **421**, 172 (1920); Michaelis and Loesner, *Ber.* **27**, 266 (1894).
[67] LaCoste, *Ann.* **208**, 5 (1881).
[68] Michaelis, *Ann.* **320**, 329 (1902).
[69] Michaelis, *Ann.* **320**, 335 (1902).
[70] Lewis and Bent, *J. Am. Chem. Soc.* **48**, 950 (1926).
[71] Hamilton and Frazier, *J. Am. Chem. Soc.* **48**, 2415 (1926).
[72] Hamilton and Griswold, Northwestern University, private communication, 1928.
[73] Hamilton and Jellinek, *J. Am. Chem. Soc.* **49**, 3168 (1927).



which takes place [74] at 110-114°, illustrates a different kind of anhydrization.

Phenyl arsonic acid [75] seems to be the only aryl arsonic acid whose decomposition has been investigated at higher temperatures. When it is heated in a sealed tube at 320°, it produces diphenyl ether, arsenic trioxide and water.

Alkyl arsonic acids have been much less studied. At 130°, methyl arsonic acid produces an anhydride which is named pyrobismethylarsonic acid, $(CH_3AsO(OH)—)_2O$, by heating [76] in a current of hydrogen, whereas at 170-180° the pyrolysis leads to the production of methanol, arsenious oxide and water:

$$2CH_3AsO_3H_2 \longrightarrow 2CH_3OH + As_2O_3 + H_2O.$$

*Iso*amyl arsonic acid [75] similarly is converted into *iso*amyl alcohol, arsenic trioxide and water by heating in a sealed tube and in an atmosphere of carbon dioxide for 4 hours at 285°.

β-Chlorovinyl arsonic acid, $ClCH=CH—AsO_3H_2$, is one of the few recorded examples of dehydration of an alkyl arsonic acid to the oxide, $ClCH=CH—AsO_2$. This occurs by heating [77] the acid at 110°. Similarly, at 110-120°, β-chloroethyl arsonic acid forms the oxide, $CH_2Cl—CH_2—AsO_2$.

Arsinic acids, $R_2As(=O)OH$, do not form anhydrides [78] on heating. Dibenzyl arsinic acid decomposes at its melting point, 210°, in accordance with the following equation: [79]

$$2(C_6H_5CH_2)_2AsO_2H \longrightarrow 2C_6H_5CHO + C_6H_5CH_2—CH_2C_6H_5 + 2As + 2H_2O.$$

Antimony.

Stibines.

The lower members of the trialkyl stibines, R_3Sb, may be distilled without decomposition, but triamyl stibine [80] undergoes a partial decom-

[74] Benda, *Ber.* **45**, 2134 (1912).
[75] Dehn, *Am. Chem. J.* **40**, 88 (1908).
[76] Baud, *Compt. rend.* **139**, 411 (1904).
[77] Mann and Pope, *J. Chem. Soc.* **121**, 1755 (1922).
[78] Raisiss and Gavron, "Organic Arsenical Compounds," New York, The Chemical Catalog Co. 1923, p. 386.
[79] Michaelis and Pactow, *Ber.* **18**, 42 (1885); *Ann.* **233**, 61 (1886).
[80] Scheibler, *J. prakt. Chem.* **64**, 505 (1855); Berlé, *Ann.* **97**, 316 (1856).

position in this process. The addition compounds of triaryl stibines with mercuric chloride quite generally decompose into arylmercuric halide and antimony trichloride, by heating in boiling alcohol:

$$Ar_3Sb.HgCl_2, \text{ or better } Ar_3Sb.3HgCl_2 \longrightarrow 3ArHgCl + SbCl_3.$$

When Ar represents phenyl, the intermediate substance is so labile that it cannot be isolated; when it represents *p*-tolyl, the decomposition occurs in hot alcohol.[81] The *o*-tolyl analog is unchanged in hot alcohol [82] but decomposes at 135°; the *m*-tolyl analog decomposes in the manner indicated in hot alcohol. Similarly, the *p*-anisyl analog, and the *p*-phenetyl analog, undergo this reaction [83] in hot alcohol.

Stibinous Oxides.

If phenyl stibinous oxide is maintained [84] at 100° for 4 hours in an atmosphere of carbon dioxide, there is a transformation into diphenyl stibinous oxide:

$$4C_6H_5SbO \longrightarrow ((C_6H_5)_2Sb)_2O + Sb_2O_3.$$

However, if the heating is conducted for 4 hours at 180-200°, the pyrolysis leads to triphenyl stibine:

$$3C_6H_5SbO \longrightarrow (C_6H_5)_3Sb + Sb_2O_3.$$

A reaction of the latter type is encountered in the pyrolysis of *m*-aminophenyl stibinous oxide, $H_2N—C_6H_4—SbO$, which gives the triaryl stibine in one hour at 120-125°.

Tri-*p*-acetylamino-triphenyl-stibine,[85] $(AcNH—C_6H_4)_3Sb$, may be synthesized by heating *p*-acetylaminophenyl-stibinous oxide, $AcNH—C_6H_4—SbO.H_2O$, for three hours in refluxing methanol with a yield, 23 grams from 50 grams. Di-*p*-acetylamino-diphenylstibinous oxide may be converted into the stibine only at 180°.

Stibinic Chlorides.

In much the manner that phosphorus pentachloride dissociates into chlorine, so phenylstibinic chloride,[86] $C_6H_5SbCl_4$, gives off chlorine by heating. The resulting phenylstibinous chloride, however, partially decomposes further and gives some antimony trichloride and diphenylstibinous chloride. If the heating is performed in a sealed tube, the chlorine recombines on cooling, giving a mixture of stibinic chlorides.

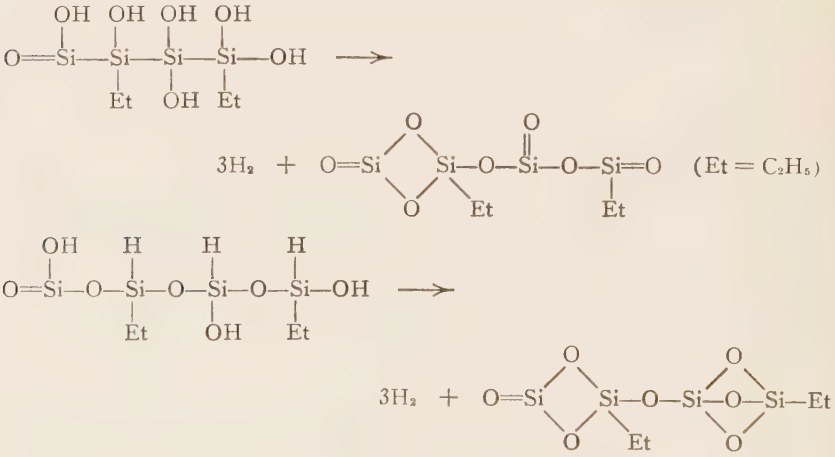
[81] Pfeiffer, *Ber.* **37**, 4622 (1904).
[82] Michaelis and Genzken, *Ann.* **242**, 176, 184 (1887).
[83] Löloff, *Ber.* **30**, 2835, 2841 (1897).
[84] Schmidt, *Ann.* **421**, 234, 242 (1920).
[85] Schmidt, *Ann.* **429**, 132 (1922).
[86] Schmidt, *Ann.* **421**, 199 (1920); Hasenbäumer, *Ber.* **31**, 2913 (1898).

p-Anisylstibinic chloride breaks down in this manner even at room temperature. By heating[87] triphenylstibine hydroxy-iodide, $(C_6H_5)_3Sb<^{OH}_{I}$, phenyl iodide is evolved.

Silicon.

The extreme thermostability[88] of silicon tetraphenyl, $Si(C_6H_5)_4$, is obvious from the fact that it boils without decomposition above 530°. The silicon analog[89] of phenyl dimethyl carbinol, $(C_6H_5)_2Si<^{CH_3}_{OH}$, is only very slowly pyrolyzed into the oxide at its boiling point. It appears *not* to give the unsaturated derivative, $(C_6H_5)_2Si{=}CH_2$, in contrast to the reaction which is so general for tertiary alcohols. It is considered that the C=Si bond is either impossible to produce, or that the conditions for its attainment must be very exceptional.

The two reactions listed below, wherein hydrogen is evolved by heating a silicon compound,[90] occur between 400° and 500°.



Metallic Carbides, and Acetylides.

The extremes of stability are represented in this class of substances. Calcium carbide is prepared at the temperature of the electric arc, and lithium carbide only decomposes above 1000°. On the other hand, cuprous acetylide, Cu_2C_2, and more particularly, silver acetylide (dry)

[87] Wilkinson and Challenger, *J. Chem. Soc.* **125**, 860 (1924).
[88] Polis, *Ber.* **18**, 1540 (1885).
[89] Kipping, *J. Chem. Soc.* **1927**, 104.
[90] Martin, *Ber.* **45**, 2097 (1912).

explode violently into the elements by warming. The detonation is due to the sudden heating of the neighboring gases. The decomposition of silver acetylide, Ag_2C_2, if pure,[91] may be made to occur with little violence, by contact with a hot glass thread. The silver salt of methyl acetylene is not explosive, but it decomposes[92] at 150° with a puff with the formation of carbon.

The monosodium derivative of acetylene[93] undergoes a complete disproportionation in a vacuum at 200-220°:

$$2Na—C{\equiv}C—H \quad (\text{or } C_2H_2.C_2Na_2) \longrightarrow Na_2C_2 + C_2H_2.$$

Sodium carbide, itself, has a dissociation pressure[94] which equals one atmosphere at 800°:

$$Na_2C_2 \text{ (solid)} \longrightarrow 2Na \text{ (gas)} + 2C.$$

The relation between the pressure and temperature has been found to follow the equation:

$$\log p = 9059 - 6609/T.$$

At sufficiently high temperatures, calcium carbide is reversibly decomposed into its elements. There is no evidence[95] of the formation of a subcarbide. Beginning at 500°, magnesium carbide forms a subcarbide:

$$2MgC_2 \longrightarrow Mg_2C_3 + C,$$

and at 600° this begins to pyrolyze[96] further into its elements.

Two forms of the cuprous salt of tertiary butyl acetylene, $(CH_3)_3C—C{\equiv}C—Cu$, are known, both of which melt[97] at 140°. There is a transition of the yellow form, which possesses the larger molecular weight, into the red form at 80°. At 150°, the yellow form gives a copper mirror and a white sublimate of tetramethyl-2,2,7,7-octadiine-3,5, $((CH_3)_3C—C{\equiv}C—)_2$. This is one case where the fusion temperature of a cuprous acetylide is below the temperature of explosion.

Other Compounds of Metals.

Cesium methylamide loses hydrogen[98] to form cesium cyanide at 120°. Since the methylamide is formed directly by the loss of hydrogen at −20° from the addition compound of cesium and methylamine, the equations for the transformations are as follows:

[91] Eggert and Schimank, *Ber.* **51**, 454 (1918).
[92] Liebermann, *Ann.* **135**, 268 (1865).
[93] Matignon, *Compt. rend.* **124**, 775 (1897); Moissan, *ibid.* **127**, 911 (1898).
[94] Guernsey and Sherman, *J. Am. Chem. Soc.* **48**, 141 (1926).
[95] Briner and Kuhne, *J. chim. phys.* **12**, 432 (1914); *Chem. Abstracts* **9**, 565 (1915).
[96] Novak, *Z. physik. Chem.* **73**, 513 (1910).
[97] Favorskii and Morev, *J. Russ. Phys. Chem. Soc.* **50**, 571 (1913); *Chem. Abstracts* **18**, 2496 (1924).
[98] Rengade, *Compt. rend.* **140**, 246 (1905).

$$2Cs(CH_3NH_2) \xrightarrow{-20^\circ} 2CH_3NH{-}Cs + H_2$$

$$2CH_3NH{-}Cs \xrightarrow{120^\circ} 2CsCN + 4H_2.$$

Similarly, it is possible [99] to form an unstable blue cesium-ethylammonium, which decomposes into cesium ethylamide, Cs—NHEt. At 105-110°, the latter undergoes pyrolysis into hydrogen, methane and ethylene. Cesium *iso*butylamide, $CsNHC_4H_9$, undergoes a complex decomposition at 110°, with evolution of hydrogen, and finally of propane and propylene.

A curious compound, copper phenyl, may be synthesized [100] by the action of cuprous iodide on phenylmagnesium bromide. At 80°, this breaks down into copper and diphenyl. If the pyrolysis is performed in boiling benzene, the yield of diphenyl is 95 percent of the theoretical:

$$2Cu{-}C_6H_5 \longrightarrow 2Cu + C_6H_5{-}C_6H_5.$$

Silver phenyl decomposes rapidly in the air to silver and diphenyl.[101]

Magnesium iodide forms a stable compound [102] with ether, $MgI_2{-}2(C_2H_5)_2O$, which melts at 52°; at 190°, ether starts to distil from it. The addition compound of ethylmagnesium iodide and ether is so stable [103] that it is only partially attacked at 100-125° in a vacuum. Grignard reagents from tertiary alcohols are, however, much less stable and frequently decompose into unsaturated compounds with astonishing ease (see pp. 194-5).

Ethyl zinc iodide is the intermediate compound [104] in the formation of zinc ethyl from ethyl iodide. To obtain zinc ethyl, the intermediate salt is heated to 180-220°:

$$2C_2H_5ZnI \longrightarrow Zn(C_2H_5)_2 + ZnI_2.$$

The addition product of ether and zinc iodide, $Et_2O{<}\overset{I\ I}{Zn}{>}OEt_2$, reverts [105] to ether and zinc iodide by heating *in vacuo* on a water bath.

The addition product of *ethyl calcium iodide* [106] and ether, $C_2H_5CaI.(C_2H_5)_2O$, gives off ether at 40° under diminished pressure.

Methyl beryllium iodide [107] also disproportionates on heating, and in this respect resembles the alkyl zinc iodides:

$$2CH_3{-}Be{-}I \longrightarrow Be(CH_3)_2 + BeI_2.$$

[99] Rengade, *ibid.* **141**, 196 (1905).
[100] Reich, *Compt. rend.* **177**, 322 (1923).
[101] Reich, *ibid.*; *see also* Krause and Wendt, *Ber.* **56**, 2064 (1923).
[102] Menschutkin, *Z. anorg. Chem.* **49**, 45 (1906); Beilstein, "Handbuch der organischen Chemie," 4th Edition, 1, 322.
[103] Blaise, *Compt. rend.* **132**, 839 (1901).
[104] Lachman, *Am. Chem. J.* **24**, 34 (1900).
[105] Blaise, *Compt. rend.* **140**, 661 (1905).
[106] Beckmann, *Ber.* **38**, 905 (1905).
[107] Gilman and Schulze, *J. Am. Chem. Soc.* **49**, 2907 (1927).

Quadrivalent tin compounds are more resistant to heat than the bivalent. Tetraphenyl tin boils above 420°, and triethyl stannic iodide boils without decomposition at 231°. By distillation (150°), diethyl tin is converted [108] in tetraethyl tin:

$$2Sn(C_2H_5)_2 \longrightarrow Sn + Sn(C_2H_5)_4.$$

The tendency of phenyl groups to wander from one tin atom to another with the formation of a higher phenylated derivative is illustrated in the following equation: [109]

$$\underset{\text{(1.5 grams)}}{2(C_6H_5)_3SnOH\cdot 1.5H_2O} \xrightarrow[\text{2 hours}]{\text{230-240° 3 mm.}} \underset{\text{(0.75 gram)}}{(C_6H_5)_4Sn} + \underset{\text{(0.1 gram)}}{4H_2O} + \underset{\text{(0.6 gram)}}{(C_6H_5)_2SnO}$$

triphenyl tin hydroxide — *tetraphenyl tin* (sublimate) — (residue) — *diphenyl tin oxide*

Diphenyl tin dihydride, $(C_6H_5)_2SnH_2$, decomposes [110] into tin diphenyl and hydrogen at temperatures above the boiling point of liquid ammonia.

Tin di-α-naphthyl melts at 200°, and it deposits [111] tin at 255°. At 205°, tin diphenyl pyrolyzes into hexaphenyl-distannane, according to the following equation:

$$3(C_6H_5)_2Sn \longrightarrow Sn + (C_6H_5)_3Sn{-}Sn(C_6H_5)_3.$$

The yield of the latter is 50 percent.

Tetramethyl lead boils at 110°, but tetraethyl lead [112] decomposes by boiling. It can be distilled in a vacuum, however, or distilled in steam. This compound, so well known at present at an anti-knock material, undergoes a monomolecular decomposition to give fine particles of free lead. This fact has been utilized in the development of theories to explain the anti-knock activity. Since a lead sol in gasoline has the same activity as a solution of lead tetraethyl,[113] this supports the idea that lead tetraethyl functions by its thermal decomposition ahead of the flame with the formation of pyrophoric particles, which then form centers for the propagation of the combustion. The same is true of iron sols and nickel sols, which have the same anti-knock activity as *iron carbonyl* or *nickel carbonyl.*

Nickel carbonyl, $Ni(CO)_4$, decomposes at 150° into nickel and carbon monoxide. At a higher temperature [114] (250-300°), the carbon

[108] Frankland, *Ann.* **85**, 340 (1853).
[109] Chambers and Scherer, *J. Am. Chem. Soc.* **48**, 1056 (1926).
[110] Chambers and Scherer, *ibid.* p. 1060.
[111] Krause and Becker, *Ber.* **53**, 175 (1920).
[112] Butlerow, *J.* **1863**, 476.
[113] Sims and Mardles, *Trans. Faraday Soc.* **1926**; *Chem. Abstracts* **20**, 2750 (1926).
[114] Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co. **1922**, paragraph 163.

monoxide is changed into carbon dioxide and carbon by the catalytic action of the nickel. Chromium carbonyl, $Cr(CO)_6$, decomposes [115] at 230° into carbon monoxide and a modification of chromium which is completely passive.

Church, Mack and Boord [116] accept the fact that in anti-knock materials such as lead tetraethyl, nickel carbonyl, cadmium dimethyl, there is pyrolysis to the free metal, and postulate that the heat evolved in the oxidation of such pyrophoric metal is a means of inducing the oxidation of the fuel. Thus, since mercury is stable in the presence of hot oxygen, mercury dialkyls cannot function as an anti-knock material.

Ethyl lead triphenyl, $(C_6H_5)_3Pb—C_2H_5$, deposits lead [117] at 235°, and lead tetraphenyl does so at 300°.[118] Zechmeister has recently reported [119] that the latter compound is stable to 240° (vacuum distillation), but at 270° lead and diphenyl are formed, together with some unchanged lead tetraphenyl. Diphenyl lead oxide, $(C_6H_5)_2PbO$, gives the same sublimates, and also a residue of lead oxide, PbO. Diphenyl lead dibromide sublimes unchanged either at the conditions of 240° or 270°. The powder from the interaction of $(C_6H_5)_2PbI_2$ and (KOH in CH_3OH) at 240° *in vacuo* gives a 35 percent yield of lead tetraphenyl. At 270° *in vacuo,* diphenyl is the substance formed, and a gray residue is left. Triphenyl lead bromide, $(C_6H_5)_3PbBr$, melts [120] at 166°, with the gradual deposition of lead bromide, $PbBr_2$.

The metallic salts of most mercaptans break down on heating [121] into the metallic sulfide and an organic sulfide. Thus, lead methyl-mercaptide, $Pb(SCH_3)_2$, changes into lead sulfide and dimethyl sulfide. The lead salt of thiophenol, $Pb(SC_6H_5)_2$, changes in a similar manner [122] at 280° into lead sulfide and diphenyl sulfide (see p. 707). The copper salts behave analogously: [123]

$$Cu(SR)_2 \longrightarrow CuS + R_2S.$$

However, mercuric mercaptides behave differently, and the pyrolysis [124] leads to free mercury and the disulfides:

$$Hg(SC_2H_5)_2 \longrightarrow Hg + C_2H_5—S—S—C_2H_5.$$

[115] Job and Cassal, *Bull. soc. chim.* **41**, 1041 (1927).
[116] Church, Mack and Boord, *Ind. Eng. Chem.* **18**, 337 (1926).
[117] Krause and Schmidt, *Ber.* **52**, 2150 (1919).
[118] Polis, *Ber.* **20**, 719 (1887).
[119] Zechmeister and Csabay, *Ber.* **60**, 1617 (1927).
[120] Grüttner, *Ber.* **51**, 1298 (1918).
[121] Klason, *Ber.* **20**, 3412 (1887).
[122] Kekulé, *Z. Chem.* **1867**, 195; Stenhouse, *Ann.* **149**, 250 (1869).
[123] Wood, Lowy and Faragher, *Ind. Eng. Chem.* **16**, 1119 (1924).
[124] Otto, *Ber.* **13**, 1289 (1880).

The synthesis of "desaurines" proceeds by a similar reaction [125] to the lead salts:

$$2C_6H_5CO{-}CH{=}C\!<\!\overset{S}{\underset{S}{>}}\!Pb \longrightarrow PbS + C_6H_5CO{-}CH{=}C\!<\!\overset{S}{\underset{S}{>}}\!C{=}CH{-}COC_6H_5.$$

MERCURY.

Previously in this monograph, the behavior of mercurous and mercuric salts of organic acids has been discussed (pp. 484-6, 494-7). Ethyl mercuric acetate, or rather a mixture of acetic acid and mercury diethyl, changes at 190° in a sealed tube [126] into mercury and ethyl acetate:

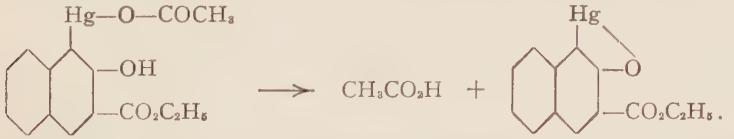
$$C_2H_5{-}Hg{-}O{-}COCH_3 \longrightarrow Hg + C_2H_5{-}O{-}COCH_3.$$

The best way to prepare mercurated benzoic acid is to heat mercuric benzoate [127] to 170°, till a sample will completely dissolve in sodium hydroxide (see p. 496):

$$(C_6H_5CO{-}O)_2Hg \longrightarrow C_6H_4\!<\!\overset{CO}{\underset{Hg}{>}}\!O + C_6H_5CO_2H.$$

The same mercurated benzoic acid [128] may also be formed by heating mercuric phthalate, in which case carbon dioxide is liberated. Usually, this reaction is performed by heating a mixture of phthalic acid and mercuric acetate.

At 150°, phenylmercuric acetate [129] changes into the following substances: carbon, mercury, benzene, acetic anhydride, acetic acid and diphenyl. Above the melting point (154°) of α-naphthylmercuric acetate, carbon is deposited,[130] and an oily residue remains. The elimination of acetic acid in the manner indicated in the following equation [131] is a characteristic reaction. In this case, the pyrolysis occurs at 100°:



Kraus [132] has isolated an interesting substance, mercury methyl, CH_3Hg, which is stable only at low temperatures; at room temperature, this decomposes into mercury and mercury dimethyl.

[125] Kelber and Schwartz, *Ber.* **45**, 139 (1912).
[126] Jones and Werner, *J. Am. Chem. Soc.* **40**, 1270 (1918).
[127] Dimroth, *Ber.* **35**, 2870 (1902); Whitmore, "Organic Compounds of Mercury," New York, The Chemical Catalog Co. **1921**, pp. 35, 290.
[128] Pesci, *Atti accad. Lincei* [5] **10**, I, 362 (1901).
[129] Dreher and Otto, *Ann.* **154**, 122 (1870).
[130] Whitmore, "Organic Compounds of Mercury," New York, The Chemical Catalog Co. **1921**, p. 201.
[131] Whitmore and Fox; thesis of A. W. Fox, Northwestern University **1927**, p. 172.
[132] Kraus, *J. Am. Chem. Soc.* **35**, 1740 (1913).

Mercury Dialkyls. Above 205°, mercury diethyl [133] changes into mercury and butane, leaving a black carbonaceous residue. This decomposition takes the form of a mild explosion. Unsymmetrical mercury dialkyls undergo disproportionation by distillation; witness, for example, the case [134] of methyl ethyl mercury:

$$2CH_3—Hg—C_2H_5 \longrightarrow Hg(CH_3)_2 + Hg(C_2H_5)_2.$$

Mercury may be completely eliminated [135] from mercury di-tertiary-butyl, $Hg(CMe_3)_2$, in 30 minutes at 40°. The isomers, mercury di-*n*-butyl and mercury di-secondary-butyl, are more stable. They are not altered in one hour at this temperature. The latter yields mercury in 2 minutes at 110°, as compared with 3-4 minutes for the former, mercury di-*n*-butyl. Mercury di*iso*amyl [136] leaves a residue of mercury by heating to 140°.

When mercury dibenzyl undergoes pyrolysis,[137] the products of the reaction are mercury and dibenzyl:

$$Hg(C_7H_7)_2 \longrightarrow Hg + C_6H_5CH_2CH_2C_6H_5.$$

If mercury dibenzyl is heated to 200° in acetic acid, mercury, toluene and benzyl acetate are formed, but, of course, the solvent in this case is not without action. Mercury di-*o,p*-dinitrobenzyl [138] loses its mercury at 235°, in accordance with the equation (see p. 495, above):

$$\underset{\textit{mercury di-o,p-dinitrobenzyl}}{Hg(CH_2—C_6H_3(NO_2)_2)_2} \longrightarrow Hg + \underset{\textit{tetranitrodibenzyl}}{(O_2N)_2C_6H_3—CH_2CH_2C_6H_3(NO_2)_2}.$$

Mercury Diaryls. Mercury diphenyl cannot be distilled [139] at ordinary pressure since it decomposes (above 300°). The products are mercury, benzene, diphenyl, carbon, and others. Similar products are obtained by passing mercury diphenyl through a glowing tube. By passing mercury di-*p*-tolyl vapors through a hot tube,[140] carbon, toluene, mercury and an oil which may be impure ditolyl are formed.

Mercury di-α-naphthyl melts at 243°. At higher temperatures, it gives rise [141] to carbon, mercury, and a brown oil that crystallizes on cooling. If mercury di-α-naphthyl is heated with soda lime, the products are mercury, naphthalene, and a substance which may be α,α′-dinaphthyl.

[133] Buckton, *Ann.* **109**, 220 (1859); Jones and Werner, *J. Am. Chem. Soc.* **40**, 1257 (1918).
[134] Frankland, *Ann.* **111**, 57 (1860). *Also* Kharasch and Grafflin, *J. Am. Chem. Soc.* **47**, 1949 (1925).
[135] Marvel and Calvery, *J. Am. Chem. Soc.* **45**, 823 (1923).
[136] Frankland and Duppa, *Ann.* **130**, 111 (1864); *J. Chem. Soc.* **16**, 415 (1863).
[137] Wolff, *Ber.* **46**, 65 (1913); Pope and Gibson, *J. Chem. Soc.* **101**, 736 (1912); Jones and Werner, *J. Am. Chem. Soc.* **40**, 1266 (1918).
[138] Kharasch, *J. Am. Chem. Soc.* **43**, 2241 (1921).
[139] Dreher and Otto, *Ann.* **154**, 97 (1870).
[140] Dreher and Otto, *ibid.* p. 171.
[141] Otto and Möries, *Ann.* **147**, 168 (1868).

Mercury di-β-naphthyl, if distilled [142] over glowing pumice, gives β,β'-dinaphthyl and other products.

The unsymmetrical mercury diaryl,[143] p-tolyl-mercury-phenyl, $\left[\mathrm{Hg}<\begin{matrix}\mathrm{C_6H_4CH_3}\\ \mathrm{C_6H_5}\end{matrix}\right]$, decomposes so readily that it cannot be isolated.

Mercuric Iodides or Sulfides. The pyrolysis of allyl mercuric iodide, $\mathrm{CH_2{=}CH{-}CH_2{-}HgI}$, into mercury, mercuric iodide and diallyl proceeds so smoothly [144] that it has been recommended as a suitable method for the synthesis of *diallyl*. Thienyl mercuric iodide,[145] , may be isolated, but it tends to pass easily into mercuric iodide and mercury dithienyl, $\mathrm{Hg(C_4H_3S)_2}$. o-Iodomercuriphenol, , melts at 125°, and above that temperature [146] decomposes in about 10 minutes into mercuric iodide and phenol.

One method of synthesis of mercury dimethyl [147] is to heat methylmercuric sulfide at 100°:

$$(\mathrm{CH_3{-}Hg{-}})_2\mathrm{S} \longrightarrow \mathrm{HgS} + (\mathrm{CH_3})_2\mathrm{Hg}.$$

Mercuric sulfide has also been reported [148] as a decomposition product of ethylmercuric sulfide, by heating. Mercury diphenyl may be formed similarly,[149] from phenylmercuric sulfide. At 160°, pentamethylenedimercuric sulfide pyrolyzes [150] and gives mercuric sulfide.

The alkyl mercuric thiosulfates,[151] $(\mathrm{RHg})_2\mathrm{S_2O_3}$, also undergo pyrolysis into mercury dialkyls.

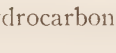
Diquinoline mercuric chloride [152] (or bromide or iodide) becomes transformed into quinoline mercuric chloride between 145° and 200°:

[142] Chattaway, *J. Chem. Soc.* **65**, 878 (1894).
[143] Hilpert and Grüttner, *Ber.* **48**, 908 (1915).
[144] Linnemann, *Ann.* **140**, 180 (1866); Oppenheim, *Ber.* **4**, 670 (1871).
[145] Steinkopf and Bauermeister, *Ann.* **403**, 57 (1914).
[146] Whitmore and Hanson; E. R. Hanson, thesis, Northwestern University, **1925**, pp. 74, 79.
[147] Hilpert and Dittmar, *Ber.* **46**, 3740 (1913).
[148] Dünhaupt, *J. prakt. Chem.* **61**, 426 (1854).
[149] Dreher and Otto, *Ann.* **154**, 116 (1870).
[150] Grüttner, *Ber.* **47**, 182 (1914).
[151] Whitmore, "Organic Compounds of Mercury," New York, The Chemical Catalog Co. 1921, p. 61, 62.
[152] Dehn, *J. Am. Chem. Soc.* **48**, 280 (1926).

CHAPTER 26.

POLYMERIZATIONS AND DEPOLYMERIZATIONS.

Polymerizations.

Saturated hydrocarbons apparently never undergo polymerization processes. Polymerization in hydrocarbons always seems to be associated with unsaturation, and this effect is particularly apparent when the substance contains conjugate double bonds; that is, —C=C—C=C—. The examples to follow will bring out the point that polymerization in such systems is not limited to the aliphatic dienes, such as butadiene or isoprene, but also includes hydrocarbons such as styrene,  , in which the conjugate nature extends to the aromatic nucleus. Because of the relationship of butadiene, isoprene and methyl isoprene to synthetic rubber,[1] great interest has been manifested in this problem of polymerization. It is included here because one of the important polymeric agencies is heat.

Two important features will be noticed in the cases of hydrocarbons which undergo polymerization. One feature, the functional group of conjugate double bonds, has been mentioned. The other is that comparatively low temperatures and long periods of time are essential. Temperatures such as 300° or 400° or 500-700° are usually entirely too severe for a successful polymerization reaction; instead, the temperatures rarely exceed 250°, and usually they are considerably below this. Although polymerization reactions are encountered in the ordinary high-temperature pyrolysis of hydrocarbons, they are usually quite secondary in nature as has been pointed out in Chapter 3. The primary effect of temperatures of about 600-700°, as measured by a short exposure of the hydrocarbon vapors to the high temperature, is one of scission into smaller products.

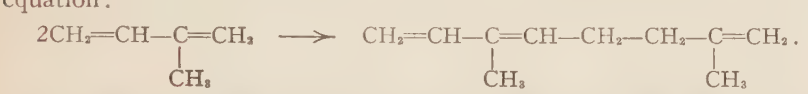
Aliphatic Dienes.

Butadiene. Patents for the conversion of butadiene to a caoutchouc-like mass by heating alone for 4 days at 90-100° in an autoclave

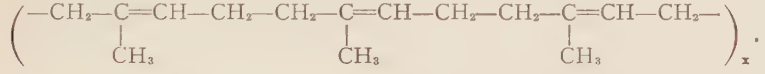
[1] For an excellent survey of the subject, *see* Schotz, "Synthetic Rubber," New York, D Van Nostrand Co., 1926.

or by heating in benzene solution for 10 hours in an autoclave at 150° have been taken out [2] by F. Bayer & Co. A rigorous survey of methods for the preparation of butadiene has been given by Ostromislensky.[3] Other means of inducing the polymerization of butadiene, particularly in the presence of other substances, are mentioned in Schotz, "Synthetic Rubber", p. 91.

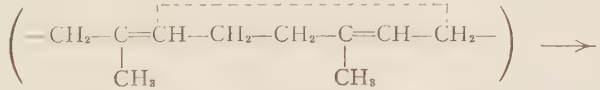
Isoprene. One of the first effects of continued heating on isoprene is to induce a dimerization into β-myrcene. Ostromislensky [4] gives the equation:



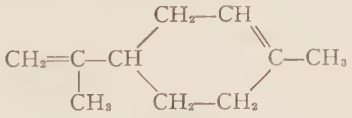
This change is brought about to a small extent by heating 1 kilo of isoprene in closed glass containers during 72-120 days at 80-90°. Most of the isoprene is still unaltered, and after distilling it away, the β-myrcene is steam distilled, dried and purified by distillation *in vacuo*. It cannot be distilled at ordinary pressures, since it becomes changed into a thin yellowish liquid. Possibly the transformation from isoprene to β-myrcene, or a closely related reaction, is the first step in the polymerization of isoprene to rubber. This would lend weight to the belief that the rubber molecule should possess a multiple formula such as:



If two units of this nucleus [5] are taken as a working basis, it is easy to see how dipentene may be one of the products. This has been actually observed [6] by heating isoprene at 280-290° for 10 hours. There is also some unchanged isoprene in this case.



the assumed formula of a polymerization unit of isoprene



dipentene

[2] Bayer & Co., D.R.P. 235,423 of 1909; Brit. Pat. 15,254, 1910; U. S. Pat. 1,069,951 and 1,070,259 1913.

[3] Ostromislensky, *J. Russ. Phys. Chem. Soc.* **47**, 1472-1506; 1947-1978 (1915); *Chem. Abstracts* **10**, 1340, 3178 (1916).

[4] Ostromislensky and Koshelev, *ibid.* **47**, 1928 (1915); *Chem. Abstracts* **10**, 1947 (1916).

[5] *See* p. 120.

[6] Bouchardat. *Compt. rend.* **80**, 1446 (1875). Tilden, *J. Chem. Soc.* **45**, 410 (1884); Wallach, *Ann.* **227**, 295 (1885).

The polymerization of isoprene to rubber has been performed by several investigators. The conditions of heating [7] in an autoclave vary from 90° to 250° and from several hours to several days. The change is, therefore, similar to the polymerization of butadiene to a solid, rubbery mass. To effect this polymerization of isoprene, Heinemann [8] suggests sealed tube heating at 100-150° for 3 days, to which catalysts may or may not be added. One of Bayer's patents [9] specifies the heating of isoprene under pressures of 4 to 20 atmospheres, preferably below 200°. Concerning the various synthetic methods which have been proposed for the polymerization of isoprene, Weil [10] makes the statement:

"It need only be said that the Hofmann heat polymerization and sodium polymerization brought out by Harries and by Matthews and Strange, and the Badische polymerization, using sodium and carbon dioxide, have been used for the manufacture of synthetic rubber. Of all these processes, however, only the heat polymerization was commercially successful. During the war synthetic rubber was made by this process on a large scale; that is, to the extent of about 150 tons per month, the total production being about 2350 tons. The only other product was a small amount made by the Badische Company by its process."

Rather in direct contradiction [11] to such a statement, however, is the one by Schotz:

"A review of the methods of polymerization can lead only to one conclusion, namely, that polymerization with the aid of metallic sodium and similar catalytic methods are the only ones of practical importance, because all others take such a long time and in consequence demand so much plant and space as to prove very troublesome in practice."

According to Lebedev,[12] the presence or absence of caoutchouc markedly influences the course of spontaneous polymerization of isoprene. The polymerization of 35 grams of the latter is stated to be complete after 3 years, if it is sealed with a small piece of caoutchouc; otherwise, at the end of three years there is still much liquid left, and only at the end of the second year is the insoluble polymer apparent. At 150°, isoprene is completely polymerized in 10 days, but the product contains only 10 percent of rubber; the chief product is dipentene.

Diolefines of widely varying formulas all polymerize similarly, but with different speeds, if conjugate double bonds are present. Lebedev observed the following speeds of polymerization, at 150°.

[7] Hofmann, *Z. angew. Chem.* **25**, 1462, 1858 (1912). For a good review of the subject, *see* Pond, *J. Am. Chem. Soc.* **36**, 188 (1914). *See also* Schotz, *loc. cit.*
[8] Heinemann, Brit. Pat. 21,772, 1907.
[9] Bayer and Co., Brit. 17 734, 1910.
[10] Richard Weil, *Ind. Eng. Chem.* **18**, 1175 (1926).
[11] Schotz, "Synthetic Rubber," New York, D. Van Nostrand & Co. 1926, p. 96.
[12] Lebedev, *J. Russ. Phys. Chem. Soc.* **45**, 1296, 1313, 1377 (1913); *Chem. Abstracts* **9**, 798 (1915).

TABLE LXII. *Speed of Polymerization of Diolefines.*

Diolefine	Time in Hours	Percent Polymeride
Isoprene	5	53
	15	79
	38	90
2,3-Dimethyl-butadiene	5	15
	15.5	about 40
	36.5	about 60
	133	87
	264	95.6
Pentadiene-1,3 (piperylene)	15	30
	40	58
Myrcene (dimethyl-3,7-octatriene-1,3,7)	4.5	53
	13.5	68
	115	78
	288	82.5
Phenyl-1-butadiene-1,3	1/12	35
	1/4	64
	1	90
Hexadiene-2,4	35	23

The polymeric product from methyl isoprene (2,3-dimethyl-butadiene) is a mixture of a dimer, related to dipentene, and a polymer. In other words, it behaves quite analogously to isoprene, differing only in a slower speed of polymerization. Harries [13] found that if 50 grams of methyl isoprene is maintained at 100° for 23 days, it yields a viscid mass, which, when freed from small amounts of terpene-like products by vacuum distillation, gives 16 grams of a caoutchouc. Most of the hydrocarbon remained unchanged. In passing, it may be stated that divinyl also gives a cyclic dimer, as well as a polymer [14] by heating to 150°. This dimer is ethenyl-cyclohexene, and it is related to dipentene as butadiene is related to isoprene. The relative yields of the dimer and of the polymer evidently depends somewhat on the particular temperature of the experiment, since Lebedev [15] observed that dimethylbutadiene gives much rubber and little of the dimer at 100°, whereas the reverse was found to be the case at 150°.

The conversion of dimethyl-butadiene into rubber by heat is covered by various patents,[16] and these include heating with or without catalysts or diluents; no yields, however, are stated. These patents deal [17] with the polymerization of compounds in general with the grouping

[13] Harries, *Ann.* **383**, 210 (1911).
[14] Lebedev and Merezhkovski, *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913); *Chem. Abstracts* **8**, 320 (1914).
[15] Lebedev, *J. Russ. Phys. Chem. Soc.* **41**, 1818 (1909).
[16] D.R.P. 250,335, 1912; and U. S. Pat. 1,074,432, 1913. *See* Schotz, *loc. cit.* p. 85.
[17] Bayer and Co. Brit. Pat. 28,850, 1910; U. S. Pat. 1,074,432, 1913.

$>C{=}C{-}C{=}C<$. An illustration is given of the polymerization of pentadiene-1,3, a cyclic compound concerning which more will be said forthwith, by heating in an autoclave for 24 hours at 150°, or 8 days at 90-100°, or 3 months at 35°. The specifications for the 4-methyl homolog indicate 12 hours at 200°.

Myrcene, which is present in bay oil, behaves in harmony with its structure, $CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$. If it is heated pyrogenically, it breaks down to isoprene in high yields.[18] If, however, it is maintained for 3 weeks at 100° under pressure, it is polymerized to a transparent viscous oil. Lebedev's results with myrcene have already been given (p. 737). Natural myrcene cannot be polymerized with such ease as β-myrcene.

Cyclic Dienes. By heating cyclopentadiene[19] in sealed tubes, a hard, brittle, white solid results which is more like porcelain than like rubber. Five polymeric products have been isolated from the solid.

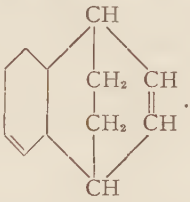
Dicyclopentadiene, $\begin{matrix} CH & CH & CH & CH \\ \| & | & | & \| \\ CH & CH & CH & CH \\ & \diagdown\diagup & \diagdown\diagup & \\ & CH_2 & CH_2 & \end{matrix}$, gives various polymers[20] by heating between 150-200°, as shown in Table LXIII.

TABLE LXIII. *Polymers of Dicyclopentadiene.*

Polymer	Percent Yield — 14 Hours 150–160°	22 Hours 170–180°	90 Hours 200°
Tricyclopentadiene	40	50	25
Tetracyclopentadiene	10	30	45
Pentacyclopentadiene	2	5	10
Polycyclopentadiene	1	2–3	15
Unchanged dicyclopentadiene	50	10	5

According to Stobbe and Reuss, cyclopentadiene is polymerized[21] by heating for 30 minutes at 135°. At least, it is certain that the rate of polymerization at temperatures of 150° is extremely rapid, more so even than isoprene. On the other hand, the rate of polymerization of 1,3-cyclohexadiene[22] at 150° is considerably slower than isoprene but is nearly the same as methyl isoprene (2,3-dimethylbutadiene). It is 46 percent polymerized in 22 hours.

[18] Prodrom, Thesis, Zurich, 1913; Schotz, *loc. cit.* p. 93. Ostromislensky was able to obtain 60-70 per cent of isoprene, by diluting myrcene with benzene, and by using Andreaff's isoprene lamp.
[19] Bruson with Staudinger. *Ind. Eng. Chem.* **18**, 381 (1926).
[20] Staudinger and Bruson, *Ann.* **447**, 97 (1926).
[21] Stobbe and Reuss, *Ann.* **391**, 151 (1912).
[22] Lebedev, *J. Russ. Phys. Chem. Soc.* **45**, 1377 (1913).

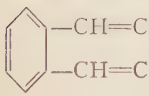
$\Delta^{1,3}$-Dihydrobenzene may be converted [23] into a thick, milky liquid by heating at 220° for ten hours either in a tube or in a copper autoclave. Distillation of the thick liquid yields up to 8 percent of the dihydrobenzene, 55-65 percent of terpene, and 40-30 percent of a rubber. Similar results may also be obtained by heating for 30 days at 120°. It is interesting to note that the pyrolysis of this dihydrobenzene rubber follows a similar course to that of ordinary rubber; thus, there is formed some $\Delta^{1,3}$-dihydrobenzene and some of its dimer,  .

Phellandrene boils at 171°, but it is reported [24] to polymerize by repeated distillations. It changes by 20 hours' heating in a tube to a glassy mass, $(C_{10}H_{16})_x$. Phellandrene possesses conjugated double bonds: C_3H_7— —CH_3.

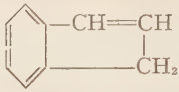
Styrene and Related Compounds.

Styrene. If styrene is heated [25] for 3 hours at 180°, or for a shorter time under pressure, it polymerizes. Apparently, benzoyl peroxide may be used to catalyze this process. The polymer may be used as a plastic. Ostromislensky states that "α, β and γ-metastyrenes" are formed [26] from either styrene or its homologs, under the influence of temperature and time. At a temperature of 300-340° and a pressure of 20-30 mm., styrene [27] pyrolyzes to naphthalene (1 percent), distyrene, and other compounds of high molecular weight.

Styrene should not be purified by ordinary distillation at atmospheric pressure since there is much loss by polymerization. To prevent this, it is advocated [27a] to add small amounts of hydroquinone as a stabilizer.

It is interesting to note that attempts [28] to prepare *o*-vinyl styrene,  , give a substance which has an extraordinary tendency to polymerize.

[23] Hofmann and Damm, *Mitt. schlesischen Kohlenforsch. Kaiser-Wilhelm Ges.* **2**, 97 (1925); *Chem. Abstracts* **22**, 1250 (1928).
[24] Pesci, *Gazz. chim. ital.* **16**, 225 (1886).
[25] Brit. Pat. 232,909, Apr. 24, 1924; 233,649, May 7, 1924; *Chem. Abstracts* **20**, 210, 649 (1926). Blyth and Hofmann, *Ann.* **53**, 311 (1845).
[26] Ostromislensky, Brit. 236,891; *Chem. Abstracts* **20**, 1243 (1926).
[27] Fischer and Treibs, *Ann.* **446**, 241 (1925).
[27a] Abbott and Johnson, *Organic Syntheses*, John Wiley and Sons, Inc., New York, 1928, vol. 8, p. 85.
[28] von Braun and Neumann, *Ber.* **53**, 109 (1920).

Indene, although bicyclic in nature, is definitely related to styrene as the formula reveals:  . At temperatures from 300-500°, indene polymerizes rapidly, when it is diluted with an inert gas. Because of this, and since indene is present in carbureted water gas, or in coal gas, resinous deposits [29] are formed in gas pipes and in gas meters unless the indene is removed. Brown found that the introduction of oxygen into the hot coal gas is effective in removing the indene.

If indene [30] is heated for 100 hours at 180-200° in a sealed tube, it gives a resinous mass, which by subsequent higher heating with a free flame produces tribenzylene-benzene (formerly called truxene). Bruson has established [31] the fact that tetraindene, $(C_9H_8)_4$, arises after 25 hours' heating in a sealed tube at 260°. In addition, a small amount of tribenzylene-benzene (yield, 0.5 gram from 25 grams) appears. If this tetraindene is either distilled at atmospheric pressure or *in vacuo,* there is produced indene, hydrindene and a 50 percent yield of tribenzylene-benzene.

The polymerization of indene by heat [32] takes place more rapidly the higher the temperature, but the molecular magnitude which is ultimately attained appears to be lower the higher the temperature. Thus, in the table which follows, the data are listed to illustrate such a statement.

TABLE LXIV. *Polymerization of Indene.*

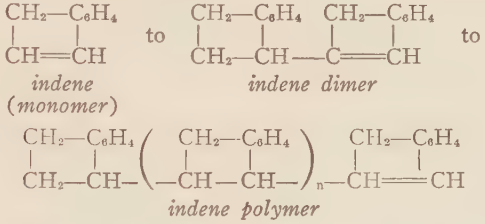
Temperature °C.	Duration of Heating Days	Extent of Polymerization Percent	Molecular Weight of Polymer	Melting Point of Polymer °C.
200	1	22.7	490	103–105
200	3	49.1	553	112–114
200	8	89.3	615	139–142
200	21	96.75	676	142–145
178	1	5.02	419	88– 90
178	3	18.55	462	97–100
178	11	65.5	566	116–118
178	30	82.2	866	158–160
140	25	15.9	414	89– 90
140	70	45.35	574	118–120
100	70	2.65	...	...

Here again, therefore, it is apparent that polymerization is essentially a low temperature process and, like most chemical reactions, the reac-

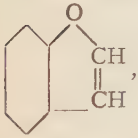
[29] Brown, *Ind. Eng. Chem.* **17**, 920 (1925); **20**, 1178 (1928).
[30] Stobbe and Zschoch, *Ber.* **60**, 473 (1927).
[31] Bruson, *Ber.* **60**, 1094 (1927).
[32] Whitby and Katz, *J. Am. Chem. Soc.* **50**, 1160 (1928).

tion is hastened by higher temperatures. The effect of too elevated temperatures, however, induces the reverse reactions of depolymerization. As Staudinger [33] has suggested, cracking sets a limit to the size of a polymeric molecule which can exist at any given temperature.

The mechanism for the polymerization of indene as suggested by Whitby and Katz involves the migration of an ethylenic hydrogen and the retention of one double bond in the molecule regardless of the molecular size; otherwise, their formulas resemble Staudinger's. Whitby and Katz demonstrate the presence of one double bond by the method of bromine absorption. Their formulation is:



Whitby and Katz also studied the pyrolytic polymerization of cinnamal fluorene, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!>\!C{=}CH{-}CH{=}CHC_6H_5$, and find that either by heating at 200° for 2 to 3 weeks, or at 240-250° for 3 days, that a polymer which is about a nonamer results. Cinnamal-indene, $\begin{matrix} CH{=}CH \\ | \quad\quad | \\ C_6H_4{-}C{=}CH{-}CH{=}CHC_6H_5 \end{matrix}$, which also contains conjugate bonds, was found to give a red, brittle resin by heating in a sealed tube at 200° for three days. The average molecular weight indicated a heptamer, but it was separated into four fractions roughly corresponding to a pentamer, hexamer, heptamer and octamer. Finally, Whitby and Katz point out that *iso*eugenol and *iso*safrole, both of which contain the semi-benzenoid conjugated systems which is also present in indene (thus, C=C—C=C), polymerize by heating at 200° far more readily than the isomeric substances, eugenol and safrole, which do not have it. This is what one would expect.

Although not an important commercial process, the cumarone,  , and the indene in solvent naphtha, boiling point 160-180°

[33] Staudinger, *Ber.* 59, 3019 (1926).

(indene content is 25-40 percent) may be polymerized [34] by heat and pressure into a resin, which is valuable either as a resin or for use in the paint and varnish industry. For such resins, however, sulfuric acid appears to be the best condensing agent.

Atropic acid, $C_6H_5—\underset{\displaystyle CO_2H}{\overset{\displaystyle |}{C}}=CH_2$, possesses the conjugate double bonds which are present in styrene, and in addition the carbonyl group is also conjugated. It polymerizes into a mixture of two isomers [35] by heating in an open dish for some time at 100-140°. Fittig recommends 24-36 hours in a sealed tube at 140-160° as the conditions to obtain good yields of polymer, which is chiefly *α-iso*atropic acid.

Acids of the sorbic series, $—C=C—C=C—\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}—OH$, polymerize easily [36] by heating as would be expected. Sorbic acid, itself, changes into a viscous, polymeric acid if it is heated at 250° in a sealed tube. The ethyl ester also changes into a thick oil at 280°.

Acrolein, $CH_2=CH—\underset{\displaystyle H}{\overset{\displaystyle |}{C}}=O$, which also has conjugated double bonds, yields an insoluble resin, disacryl,[37] on standing. The reaction is hastened by both heat and light.

Chinese wood oil, which consists essentially [38] of the glyceride of eleomargaric acid, $CH_3—(CH_2)_3—CH=CH—CH=CH—(CH_2)_9—CO_2H$, dimerizes in one hour at 220°. Continued heating (360°) induces further polymerization, and eventually the oil sets to a jelly in which the dimer is enmeshed in the precipitated higher polymer. The dimer is stated to be a substance wherein the two component glyceride molecules are joined by a single tetramethylene linkage, formed by the condensation of one pair of ethenoid groupings. Linolenic monoglyceride appears to undergo isomerization [39] at 225°, and at 250° coupling and condensation reactions occur. In 84 minutes at 250°, the oil becomes a gel. During this process the hexabromide number decreases steadily and reaches a small value by the time gelation occurs. Linseed and perilla oils take a much longer time to gel at this temperature, and the hexabromide becomes zero long before gelation occurs. The gel is thought to be either a dimer or a higher polymer. At the moment of gelation, the gel from linolenic monoglyceride has a molecular weight of 1700-

[34] Schotz, "Synthetic Organic Compounds," London, Ernest Benn, Ltd., 1924, p. 349.
[35] Fittig and Wurster, *Ann.* **195**, 149 (1879); Fittig, *Ann.* **206**, 34 (1881).
[36] Doebner, *Ber.* **35**, 2129, 2538 (1902).
[37] Moureu and Dufraisse, *Compt. rend.* **169**, 621 (1919).
[38] Rhodes and Welz, *Ind. Eng. Chem.* **19**, 73 (1927).
[39] Long, Egge and Wetterman, *Ind. Eng. Chem.* **19**, 903 (1927).

1800. At 293°, linolenic monoglyceride rapidly pyrolyzes, and acrolein, carbon dioxide and water have all been detected.

Diethyl muconate,[40] $EtO_2C{-}CH{=}CH{-}CH{=}CH{-}CO_2Et$, undergoes polymerization by heating for 5 hours in a tube at 180°. Fractionation of this material at 1 mm. (208-230°) yields a dimer,

$$\begin{array}{l} EtO_2C{-}CH{-}CH{=}CH \\ \quad\quad\quad\quad\quad\quad | \quad\quad\quad | \\ EtO_2C{-}CH{-}CH{-}CH{-}CO_2Et \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad CH{=}CH{-}CO_2Et \end{array}$$

, and a pitch-like residue.

Vinyl acetate may be prepared[41] by the interaction of acetylene and acetic acid. Under the influence of light or catalysts, this may be converted into a polymeric resin which is capable of being hydrolyzed by alcoholic sodium hydroxide into a polyvinyl alcohol. The polymerization of vinyl acetate[42] may be initiated by heating under a reflux which is then withdrawn and the polymerization is completed in another vessel. Simultaneously, a new cold portion is added to the reflux apparatus (see p. 530). Polyvinyl alcohol[43] is an interesting substance to which Staudinger ascribes the formula:

$$\begin{array}{l} -CH{-}CH_2{-}\left(\begin{array}{l} -CH{-}CH_2{-} \\ \quad | \\ \quad OAc \end{array}\right)_x{-}CH{-}CH_2{-} \\ \quad | \quad\quad\quad\quad\quad\quad\quad | \\ \quad OAc \quad\quad\quad\quad\quad\quad\quad OAc \end{array}$$

($x = 40$ to 100)

The substance resembles starch in its reaction with a solution of iodine in potassium iodide, but it is a more stable substance than starch. This carbohydrate-like substance is not altered at 150° and 30 atmospheres pressure, but at 200-220° it changes into a very hard, horny mass of the same composition but of different solubilities.

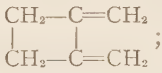
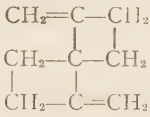
Allyl furfuracrylate[44] polymerizes after a 34 hour period of heating in an evacuated tube at 210°. The polymer, on heating by itself, swells and forms a glassy, solid, brittle mass.

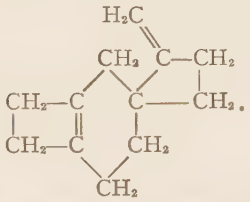
Allenes and Ketenes.

Substances of this type possess a different type of unsaturation from that which has been mentioned above; thus, either C=C=C or C=C=O. Allene, itself, polymerizes fairly rapidly[45] by heating under pressure. By heating allene to 140° in Ipatiew's high-pressure apparatus

[40] Vogt, *Mitt. schlesischen Kohlenforsch. Kaiser-Wilhelm Ges.* **2**, 69 (1925); *Chem. Zentr.* **1926**, I, 2340; *Chem. Abstracts* **21**, 3890 (1927).
[41] Staudinger, Frey and Starck, *Ber.* **60**, 1782 (1927).
[42] Brit. 261,406, Nov. 14, 1925; *Chem. Abstracts* **21**, 3369 (1927).
[43] Staudinger, Frey and Starck, *loc. cit.*; Hermann and Haehnel, *Ber.* **60**, 1658 (1927).
[44] Blicke, *Ber.* **47**, 1352 (1914).
[45] Lebedev, *J. Russ. Phys. Chem. Soc.* **45**, 1357 (1913); *Chem. Abstracts* **9**, 798 (1915); Lebedev and Merezhkovski, *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913); *Chem. Abstracts* **8**, 322 (1914).

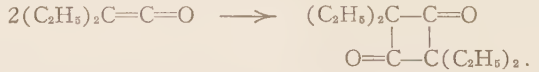
(metallic), the pressure was found to fall in 3 days from 58 mm. to 16 mm., and the hydrocarbon was converted in part to a semi-solid mass, resembling caoutchouc. In a sealed glass tube, one-half of the allene polymerizes in 3.5 days at 140°, giving 5 percent of a dimer, 15 percent of a trimer, 5 percent of an α-tetramer and 22 percent of a β-tetramer, 18 percent of a pentamer, 10 percent of a hexamer, and 25 percent of a gummy residue. Lebedev suggests the following formulas:

the dimer,  ; the trimer,  ; the two isomeric

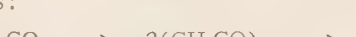
tetramers,  .

Lebedev found that symmetrical dimethyl allene changes into a dimer at 150°, and that in general the allene hydrocarbons (aliphatic) polymerize more easily than those of the divinyl type. Unsymmetrical dimethyl allene has a speed of polymerization at 150° that is very similar to that of isoprene.

If diethyl ketene [46] is kept in a sealed tube at 100° for 6 days, it becomes transformed into tetraethyl-diketo-cyclobutane:



To prevent [47] the polymerization of dimethyl ketene, it must be cooled to —80° (see p. 577). Ketene readily polymerizes on standing, and gives rise to cyclobutane-dione; the latter [48] if kept at 80-90° for a few hours changes into dehydroacetic acid. Empirically, this may be represented as follows:



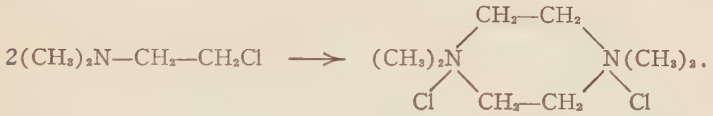
Staudinger and Rathsam [49] have shown that if phenyl-ketene acetal, $C_6H_5—CH=C(OC_2H_5)_2$, is maintained for 6 hours at 260-270° the ketene acetal polymerizes, and gives ethyl phenylacetate and a colorless solid.

[46] Staudinger and Maier, *Ann.* **401**, 292 (1913); *see also*, Staudinger and Ott, *Ber.* **41**, 2208, 3829 (1908).
[47] Staudinger, Felix and Harder, *Helv. Chim. Acta* **8**, 306 (1925).
[48] Chick and Wilsmore, *J. Chem. Soc.* **97**, 1996 (1910); Staudinger, "Die Ketene," Stuttgart, F. Enke 1912, p. 38, ff.
[49] Staudinger and Rathsam, *Helv. Chim. Acta* **5**, 645 (1922).

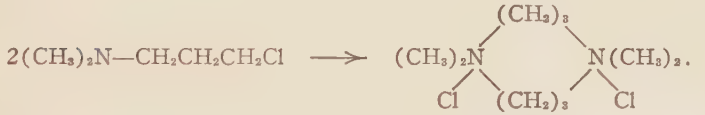
The polymerization of acetylene to benzene is still another type of polymerization. This has been treated in Chapter 3.

Diallyl is a 1,5-diene, $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$. It is therefore of a still different type. Lebedev [50] found that if it is heated for 8 days at 140-200° there is still unchanged hydrocarbon. In 10 days at 250°, there is formed a crude product which is about 15 percent liquid dimer, and 85 percent of an insoluble, rubbery mass.

The formation of diethylene-bis-piperidinium chloride, mentioned on page 45, is polymerization but obviously is quite different in nature. This is formed [51] by heating *N*-β-chloroethyl-piperidine in hot alcohol. Many β- and γ-chloroamines polymerize on standing. Thus: [52]



and



Depolymerizations.

Tervalent Carbon and Divalent Nitrogen.

No attempt will be made in this monograph to present a complete survey of triphenylmethyl and related compounds. However, the dissociation of hexaphenylethane into triphenylmethyl is one which is influenced by the temperature, although it must be recognized that the nature of the solvent also affects the extent of the dissociation. In addition to a great variety of triarylmethyls which have been studied in particular by Gomberg, recent work [53] has also established that tetraphenyl dicyano ethane begins to dissociate [54] into free radicals at 140°, and the tetraanisyl compound [55] at 60-80° depending on the solvent. The dibenzoyl derivative of benzoyl pinacol behaves similarly. Conant [56] has demonstrated the effectiveness of secondary alkyl groups in promoting the dissociation of dixanthyl derivatives.

Kharasch [57] has reasoned that the electronegativity of the substituent

[50] Lebedev, *J. Russ. Phys. Chem. Soc.* **45**, 1372 (1913); *Chem. Abstracts* **9**, 798 (1915); **8**, 323 (1914).
[51] Knorr, Hörlein and Roth, *Ber.* **38**, 3136 (1905).
[52] Knorr, *Ber.* **37**, 3507 (1904); Knorr and Roth, *Ber.* **39**, 1420 (1906); von Braun, *Ann.* **386**, 297 (1912).
[53] For a survey of the topic to 1914, *see* Gomberg, *J. Am. Chem. Soc.* **36**, 1144-1170 (1914).
[54] Löwenbein and Gagarin, *Ber.* **58**, 2643 (1925).
[55] Blicke, *J. Am. Chem. Soc.* **47**, 1477 (1925).
[56] Conant, Small and Sloan, *ibid.* **48**, 1743 (1926).
[57] Kharasch and Marker, *ibid.* **48**, 3139 (1926).

radical on an ethane nucleus is the factor of prime importance in a study of these dissociations. Two identical alkyl groups are more loosely held by the binding pair of electrons, the less electronegative they are. Illustrated with ethane and with hexaphenylethane, the formulas become

$$H_3C : CH_3$$
$$(C_6H_5)_3C : C(C_6H_5)_3$$

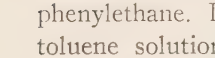
With a radical, X, which possesses still greater electron attraction than phenyl, then the radical, CX_3 must exert less attraction for its electrons than $C(C_6H_5)_3$, and the new formula may be pictured:

$$X_3C : CX_3$$

Expressed in words, the more loosely these two radicals are joined, the greater is their tendency for dissociation (see Chapter 2).

Diphenyl nitrogen, $(C_6H_5)_2N$, is related to tetraphenyl hydrazine (see p. 631) in the same manner that triphenylmethyl is to hexaphenylethane. Hexaphenyltetrazane,[58] $(C_6H_5)_2N—N(C_6H_5)—N(C_6H_5)—N(C_6H_5)_2$, shows the greatest tendency of any known compound to dissociate into bivalent nitrogen radicals.

It is interesting to note that di-*tert.* butyl-tetraphenylethane,[58a]



undergoes dissociation in the manner of hexaphenylethane. Its original molecular weight in a 5 percent *p*-chlorotoluene solution is 390. This value drops to 227 after 12 minutes' heating at 100°. The theoretical value for complete cleavage is 223.

In these cases of depolymerization, the unsaturation in the compound is centralized at one atom. In the cases to follow, the depolymerized compounds are also unsaturated, but the unsaturation is shared by at least two atoms. This is depolymerization in the usual sense.

Polymers of Unsaturated Compounds.

Para-anthracene melts with depolymerization into anthracene[59] at 243° (or 272°, Elbs). *Dicyclopentadiene* (*α*- or *β*-) changes into cyclopentadiene[60] at 170-180°. The effect of continued heating under pressure in promoting polymerization instead of depolymerization has been mentioned on page 738. Tetrahydro-dicyclopentadiene is more resistant towards heat than dicyclopentadiene. It requires a red-hot tube for its

[58] Goldschmidt and Euler, *Ber.* **55**, 616 (1922).
[58a] Conant and Bigelow, *J. Am. Chem. Soc.* **50**, 2044 (1928).
[59] Graebe and Liebermann, *Ann. Supp.* **7**, 264 (1870); Elbs, *J. prakt. Chem.* [2] **44**, 467 (1891).
[60] Stobbe and Reuss, *Ann.* **391**, 154 (1912); Staudinger and Rheiner, *Helv. Chim. Acta* **7**, 23 (1924). For addresses on polymerization and depolymerization, *see* Staudinger, *Ber.* **59**, 3019 ff. (1926).

depolymerization. *Bis-indene* [61] may be distilled in a high vacuum, but at atmospheric pressure, distillation gives indene:

$$C_{18}H_{16} \longrightarrow 2C_9H_8.$$

Tri-indole, $(C_8H_7N_3)_3$, melts at 167° and it is quantitatively reverted [62] into indole by vacuum distillation. Monobenzoyl-triindole undergoes a rather remarkable smooth decomposition into indole and benzoyl-diindole by heating in a vacuum. A polymer of cumarone, namely, *cumarone-resin,* which is made by treating cumarone with sulfuric acid, gives [63] about a 20 percent yield of cumarone by dry-distillation (300-350°). The remainder becomes further pyrolyzed to phenol, carbon and other substances:

$$\longrightarrow C_6H_5OH + 2C, \text{ etc.}$$

Cumarone, however, is very resistant [64] to heat. From 100 grams, passed through a tube at red heat, 94 grams was recovered.

Styrene becomes polymerized [65] to *meta*-styrene by heating in a sealed tube at 200°; in turn, *meta*styrene changes into styrene by distillation. Anisalacetophenone possesses the unsaturation of styrene, and in addition a conjugated carbonyl group. Above its melting point, 76°, it changes [66] into a red resin although it is unchanged by rapid distillation. A dimer of this substance, formed in the presence of ultra-violet light on the solid, undergoes pyrolysis in two directions by dry distillation. One is a depolymerization to the original anisalacetophenone, and the other leads to the formation of *p,p'*-dimethoxy-stilbene.

$CH_3O\ C_6H_4—CH{=}CH—CO—C_6H_5$
anisalacetophenone

$$CH_3O—C_6H_4—CH—CH—COC_6H_5$$
$$\quad\quad\quad

acid has been studied rather carefully [68] for its products of distillation, chief of which are stilbene and trans-cinnamic acid. It is of interest to record the following data, taken during the pyrolysis of 120 grams of α-truxillic acid. The weight of the distillate between 90-190° is 1.6 grams (liquid); between 190-290°, 26.6 grams, chiefly trans-cinnamic acid; between 290-320°, 50.7 grams, composed of stilbene, a solid of melting point 192°, γ-truxillic anhydride, η-truxillic anhydride, and some distyryl. Above 320° 3.4 grams of a mixture of tar and water distils. There is 18.1 grams of residue.

A comparative run with *trans*-cinnamic acid (50 grams) yields 30 grams of cinnamic acid and 3 grams of a stilbene-styrene mixture below 280°; at 280-310°, one gram of a resinous mass distils over and leaves 8 grams of carbonized residue. β-Truxillic acid, like the α-, gives stilbene [69] instead of distyrene in the distillate.

The destructive distillation of india rubber has been treated in an earlier chapter. Suffice it to remark at this point that Williams,[70] who recognized that isoprene was more than a pyrolytic product of rubber, considered nearly seventy years ago: "the action of heat on caoutchouc to be merely the disruption of a polymeric body into substances having a simple relationship to the parent hydrocarbon".

If cyclic dibutene,[71] , is subjected to a temperature of 500-600° and 100 mm. pressure by means of an isoprene lamp, it is decomposed into two molecules of butadiene. One of the more important components of oil of turpentine is pinene, a bicyclic hydrocarbon of formula $C_{10}H_{16}$. Many investigators have been interested [72] in the possibility of obtaining isoprene, C_5H_8, by pyrogenic decomposition of pinene or related terpenes. According to Prodrom and Staudinger, the decomposition *in vacuo* at high temperatures gives the following components: crude distillate, 42 percent; crude isoprene, 25 percent; residue, 44 percent; losses due to gas, 14 percent. Monocyclic terpenes, such as dipentene are much more suitable for isoprene production by this method. Staudinger and Klever [73] found that if the vapors of dipentene in high dilution with nitrogen, or in a vacuum of 2-3 mm., are passed over a hot platinum coil, decomposition occurs with the formation of 60 percent of isoprene. For the reverse process, see page 735.

[68] Stobbe and Zschoch, *Ber.* **56**, 676 (1923).
[69] Liebermann, *Ber.* **43**, 1543 (1910).
[70] Williams, *Proc. Roy. Soc.* (London) **10**, 516 (1860).
[71] Ostromislensky, *J. Russ. Phys. Chem. Soc.* **47**, 1947 (1915); *Chem. Abstracts* **10**, 1340, 3178 (1916).
[72] Schotz, "Synthetic Rubber," New York, D. Van Nostrand Co. 1926, p. 15. Prodrom, with Staudinger, Thesis, Zurich, 1913.
[73] Staudinger and Klever, *Ber.* **44**, 2212 (1911).

Supniewski has recently reported [74] a yield of 100 grams of pure isoprene from 300 grams of limonene by the use of the isoprene lamp. In addition, he reported about 80 grams of a mixture containing limonene. From turpentine, he was only able to obtain a 4-5 percent yield of pure isoprene.

Aldehyde Polymers.

It is difficult to keep pure *formaldehyde* from polymerizing. Therefore, in many reactions, such as the synthesis of primary alcohols by the Grignard reaction, formaldehyde is prepared by depolymerization of paraformaldehyde and the gaseous formaldehyde is used at once. For this purpose, paraformaldehyde which has been dried over P_2O_5 for two days is placed in a flask which is heated [75] by an oil bath at 160-200°. The aldehyde passes from the flask in a steady stream. A practical application of this pyrogenic depolymerization is the formaldehyde candle.

Metaldehyde becomes completely depolymerized [76] into acetaldehyde by heating at 200° in a sealed tube; the polymer sublimes by heating in the open. However, if the metaldehyde vapors are passed [77] through a hot tube, acetaldehyde is formed, part of which pyrolyzes further into methane and carbon monoxide. If paraldehyde is brominated at −15° to −10°, a 60-87 percent yield of *dibromoparaldehyde,* boiling point (10 mm.) 126°, results. This substance breaks down [78] at 155° into $CH_3CHO + 2CH_2Br—CHO$.

These aldehyde polymers are *O*-heterocyclic compounds. *Polyglycollide,* presumably also an *O*-heterocyclic substance, which is formed by the pyrolysis of glycollic acid at 240-280°, changes into diglycollide, $\begin{matrix} CH_2—O—CO \\ | \quad\quad | \\ CO—O—CH_2 \end{matrix}$, by vacuum distillation.[79]

A thermal disintegration of recent interest [80] is the transformation of tetraamylose acetate into diamylose acetate, by heating in 20 parts of naphthalene for an hour between 150-200°. The yield is about 50 percent.

Ingold and Piggott have studied the system:

$$A{=}B + C{=}D \rightleftharpoons \begin{matrix} A—B \\ | \quad | \\ C—D \end{matrix} \rightleftharpoons A{=}C + B{=}D,$$

[74] Supniewski, *Roczniki Chem.* **7**, 176 (1927); *Chem. Abstracts* **22**, 941 (1928).
[75] Noller and Adams, *J. Am. Chem. Soc.* **48**, 1085 (1926); "Organic Syntheses," Vol. VI, New York, John Wiley and Sons, Inc., 1926, p. 23.
[76] Burstyn, *Monatsh.* **23**, 737 (1902).
[77] Peytral, *Bull. soc. chim.* **27**, 34 (1920).
[78] Stepanow, Preobraschensky and Schtschukina, *Ber.* **58**, 1720 (1925).
[79] Bischoff and Walden, *Ber.* **26**, 263 (1893); Anschütz, *ibid.* p. 560.
[80] Pringsheim and Meyersohn, *Ber.* **60**, 1714 (1927).

as applied to Schiff's bases, Ar—CH=N—Ar'. Their results [81] lend confirmatory evidence for the following hypothesis: In double-bonded compounds, there exists a general tendency towards the establishment, in the liquid state or in solution, of an equilibrium with the dimeric form;

$$2A{=}B \rightleftharpoons \begin{matrix} A{-}B \\ | \quad | \\ B{-}A \end{matrix}$$

The division of the cyclic compound is a process which resembles depolymerization. This is illustrated in the pyrolysis of 3-*p*-bromophenyl-2-*p*-hydroxyphenyl-1,4-diphenyl-1,3-dimethindiazidine, which occurs rather rapidly at its melting point, 165-167°, or by heating in alcohol.

$$HOC_6H_4{-}CH{=}N{-}C_6H_5 + C_6H_5CH{=}N{-}C_6H_4Br \longrightarrow \begin{matrix} HO{-}C_6H_4{-}CH{-}N{-}C_6H_5 \\ | \quad | \\ Br{-}C_6H_4{-}N{-}CH{-}C_6H_5 \end{matrix}$$

$$\begin{matrix} HO{-}C_6H_4{-}CH{-}N{-}C_6H_5 \\ | \quad | \\ Br{-}C_6H_4{-}N{-}CH{-}C_6H_5 \end{matrix} \longrightarrow HO{-}C_6H_4{-}CH{=}N{-}C_6H_4Br + C_6H_5CH{=}N{-}C_6H_5$$

Similarly, the dimethindiazidine, formed from $HOC_6H_4{-}CH{=}N{-}C_6H_5$ and *m*—$O_2N{-}C_6H_4{-}N{=}CHC_6H_5$, that is,

$$\begin{matrix} HOC_6H_4{-}CH{-}N{-}C_6H_5 \\ | \quad | \\ O_2NC_6H_4{-}N{-}CHC_6H_5 \end{matrix}$$

divides into benzalaniline, $C_6H_5CH{=}NC_6H_5$, and *p*-hydroxybenzal-*m*-nitraniline, $HOC_6H_4CH{=}NC_6H_4NO_2$. Ingold cites other similar cases, in many of which it is not possible to isolate the intermediate dimethindiazidine. One striking feature of these changes, not mentioned by Ingold, is that the division of the cyclic compound invariably makes for greater symmetry. Thus, benzalaniline is the invariable product if two phenyl groups are present, as in the cases cited. In the reaction:

$$(m\text{- or } p\text{-})\text{-}O_2N{-}C_6H_4CH{=}N{-}CH_2C_6H_5 + (m\text{- or } p\text{-})\text{-}O_2N{-}C_6H_4CH_2{-}N{=}CHC_6H_5,$$

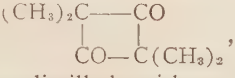
the reaction products invariably are:

$$O_2NC_6H_4CH{=}N{-}CH_2C_6H_4NO_2 + C_6H_5CH_2{-}N{=}CHC_6H_5.$$

Here also, the tendency of the nitrophenyls is to become associated in the same compound, and promote symmetry. Other causes may also appear in this change. Admittedly, little is known concerning symmetry in promoting change.

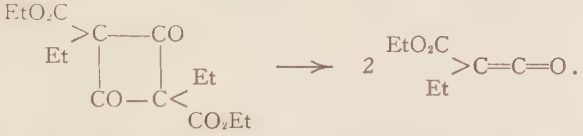
[81] Igold and Piggott, *J. Chem. Soc.* **121**, 2793 (1922).

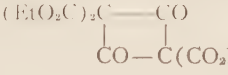
KETENE POLYMERS AND RELATED COMPOUNDS.

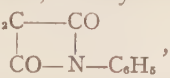
The simplest polymers of the ketenes are the cyclobutanediones. The diaryl ketenes do not polymerize, but most of the dialkyl ketenes gradually change into dimers at room temperature. In most cases, the depolymerization reaction may be induced by distillation. Tetramethyl-cyclobutanedione,[82]  , exhibits a high order of stability. It may be distilled without decomposition. 1,3-Dimethyl-cyclobutanedione is less stable, and cyclobutanedione is the least stable of these three compounds. Dickens, Kon and Thorpe[83] have taken cognizance of this decreasing order of stability in their studies on the central angle of a three carbon system.

A polymer of dimethyl ketene with a molecular weight of over 2000 may be prepared[84] by the action of trimethylamine in ether. If heated, this polymer reverts to dimethyl ketene, the temperature of depolymerization depending on the temperature of formation of the polymer. If made at −80°, the polymer decomposes above 200°; if prepared at + 20°, it yields dimethyl ketene at 110-150°.

The dimer of ethyl ketene carboxylic ester boils[85] at 113-116° in a vacuum of 0.16 mm., but at 15-20 mm. it depolymerizes at 180-200°:



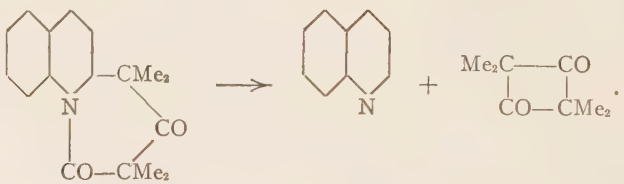
On standing for a time, the ketene changes very smoothly into the dimer. Tetra-carbethoxy-cyclobutanedione,[82]  , distils without depolyerization only in an absolute vacuum.

Ketenes attach themselves to other unsaturated compounds by a process that resembles polymerization, and these reactions are usually reversible at higher temperatures (see p. 577). Thus, the cyclic compound, diphenylmalonic acid phenyl-imide,[86]  , from diphenyl ketene and phenyl *iso*cyanate, yields phenyl *iso*cyanate again at 300-330°.

[82] Staudinger, *Helv. Chim. Acta* **7**, 3 (1924).
[83] Dickens, Kon and Thorpe, *J. Am. Chem. Soc.* **121**, 1496 (1922).
[84] Staudinger, Felix, Meyer and Harder, *Helv. Chim. Acta* **8**, 322 (1925).
[85] Staudinger and Bereza, *Ber.* **42**, 4908 (1909).
[86] Staudinger, Göhring and Schöller, *Ber.* **47**, 41, 46 (1914).

Pentaphenyl nitrene,[87] $(C_6H_5)_2C{=}N{=}C(C_6H_5)_2$ with C_6H_5 below the N, adds a molecule of diphenyl ketene and the constituents are restored by heating. This nitrene also attaches hydrogen chloride, but above the melting temperature, 163°, hydrogen chloride is liberated. The addition compounds of aryl ethylenes to diphenyl ketene, $(C_6H_5)_2C{-}{-}CH_2$ / $CO{-}CH{-}Ar$, undergo complete pyrolysis[88] into the olefine and diphenyl ketene at temperatures below 200°. The radical Ar may represent C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$, and the respective temperatures of decomposition are 200° *in vacuo,* 171° (melting point), 120° (melting point), and "gentle heating". The addition compounds from cyclohexane and cyclopentadiene behave similarly, but the one from cyclopentene is only gradually decomposed[89] by heat into its parts.

Quinoline absorbs 2 mols of dimethyl ketene to form a compound which is unaffected by heating for 3 hours at 150-200°, but it changes into quinoline and tetramethyl-cyclobutanedione after several hours' heating[90] at 250°:



A similar compound from quinoline and diphenyl ketene changes into a dark colored melt[91] after 8 hours at 200°.

Staudinger considers[92] the interaction of phenyl *iso*cyanate and *p*-dimethylaminobenzaldehyde at 190° to be analogous to the interaction of *iso*cyanates and ketenes, differing only in the stability of the addition product. In this case then, the mechanism would assume an intermediate cyclic compound which would undergo pyrolysis:

$$\left[\begin{array}{c} C_6H_5{-}N{-}{-}CO \\ | \quad\quad | \\ (CH_3)_2NC_6H_4{-}CH{-}O \end{array}\right] \longrightarrow (CH_3)_2NC_6H_4{-}CH{=}N{-}C_6H_5 + CO_2.$$

This viewpoint is related intimately to that of Ingold and Piggott, which was set forth on page 750.

[87] Staudinger and Miescher, *Helv. Chim. Acta* **2**, 554 (1919).
[88] Staudinger, *Ber.* **53**, 1073 (1920); Staudinger and Suter, *ibid.* p. 1092.
[89] Staudinger and Rheiner, *Helv. Chim. Acta* **7**, 8 (1924).
[90] Staudinger, Klever and Kober, *Ann.* **374**, 19 (1910).
[91] Staudinger, *Ann.* **356**, 111 (1907).
[92] Staudinger and Endle, *Ber.* **50**, 1042 (1917).

There seem to be at least two polymers of diphenyl ketene oxide, $(C_{14}H_{10}O_2)_x$. The higher melting material pyrolyzes [93] at 200-210° by rapid heating, giving carbon dioxide, benzophenone and diphenylacetic acid. If it is heated at 140-160° in ether, these products are also formed, but in addition, benzilide appears. The structure of benzilide (p. 433) is: $(C_6H_5)_2C(-O-CO)C(C_6H_5)_2$ (O bridging the two carbons, CO bridging the two carbons). Its relationship to diphenyl ketene oxide is apparent. The lower melting oxide behaves similarly, but the pyrolysis starts at a lower temperature; namely, at 120-130° by slow heating and 160-180° by rapid heating.

Cyanate Polymers.

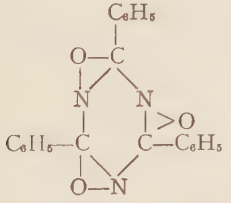
The fact that cyanic acid polymerizes to a mixture of cyanuric acid and cyamelide has been set forth in the chapter on urea. Also, it has been related how cyanuric acid reverts into cyanic acid by distillation. Another polymer, pentacyanic acid, $(HNCO)_5$, melts at 148°, and yields [94] cyanic acid at 370°.

Triethyl cyanurate [95] also yields cyanic acid by pyrolysis when the vapors are passed in a high vacuum over a platinum spiral at dull red heat:

$$(C_2H_5NCO)_3 \longrightarrow 3C_2H_4 + 3HNCO.$$

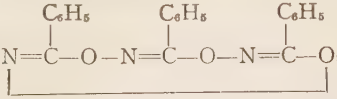
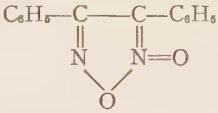
Methoxymethyl *iso*cyanate is an oil which polymerizes [96] in a few days to a vitreous solid.

A dimer of phenyl *iso*cyanate, $C_6H_5N{<}^{CO}_{CO}{>}NC_6H_5$, melts [97] at 175°; above this temperature, diphenyl di*iso*cyanate reverts into phenyl *iso*cyanate. Benzonitrile oxide, C_6H_5CNO, melts at 15° and resolidifies [98] into a trimer. If this is heated in toluene, it depolymerizes, but instead of reverting to the nitrile oxide, it changes into phenyl *iso*cyanate:

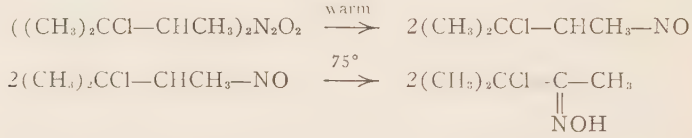


$$\longrightarrow 3C_6H_5{-}N{=}C{=}O.$$

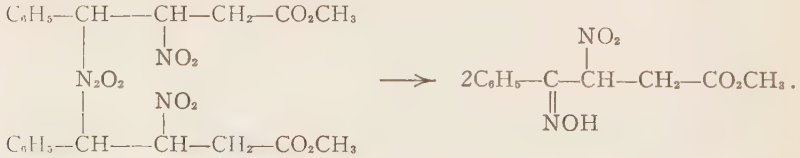
[93] Staudinger and others, *Ber.* **58**, 1079 (1925).
[94] Salomone, *Gazz. chim. ital.* **42**, 1, 621 (1912).
[95] Kesting, *J. prakt. Chem.* **105**, 242 (1923).
[96] Jones and Powers, *J. Am. Chem. Soc.* **46**, 2518 (1924).
[97] Hofmann, *Ber.* **4**, 247 (1871).
[98] Wieland, *Ber.* **42**, 815 (1909).

Pauling and Hendricks [99] think that the polymer possesses a 9-membered ring,  , and that in the pyrolysis the phenyl group wanders from the carbon to the adjacent nitrogen atom. A related compound, diphenyl furoxane,  , may be regarded [100] as a dimer of benzonitrile oxide, although it is not synthesized from it. Instead, it is prepared from benzil dioxime by oxidation. By rapid distillation, this compound also changes (by rearrangement) into phenyl *iso*cyanate.

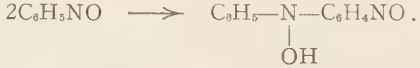
The familiar conversion of the colorless, dimolecular nitroso compounds into the blue, monolecular nitroso compounds is one which depends on the temperature. One illustration,[101] interesting because it also shows the rearrangement to an oxime, is given in the following steps:



The pseudonitrosite [102] of methyl phenyl*iso*crotonate undergoes a smooth transformation by refluxing in absolute alcohol for 30 minutes.



Nitrosodiphenyl-hydroxylamine [103] is a polymer of nitrosobenzene which is formed by contact with concentrated sulfuric acid at 0°:



It melts with effervescence at 147-152° to a brown liquid, the nature of which has not been determined.

[99] Pauling and Hendricks, *J. Am. Chem. Soc.* **48**, 648 (1926).
[100] Auwers and Meyer, *Ber.* **22**, 717 (1889); Wieland and Semper, *Ann.* **358**, 53 (1908).
[101] Schmidt, *Ber.* **35**, 3728 (1902).
[102] Wieland, *Ann.* **329**, 251 (1903).
[103] Bamberger, Büsdorf and Sand, *Ber.* **31**, 1513 (1898).

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